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COMPLETE SPECIFICATION

Improvements in or relating to Antiseptics and Disinfectants

We, RECKITT & SONS LIMITED, a British Company, of Dansom Lane, Hull, Yorkshire, SYDNEY NORMAN HERBERT STOTHART, a British Subject, of 51, Allderidge Avenue, Hull, Yorkshire, and GEOFFREY CHARLES BEECROFT, a British Subject, of 15, Cayton Road, Hull, Yorkshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is for improvements in or relating to antiseptics and disinfectants.

It is an object of the present invention to provide antiseptic and disinfectant fluids for animals and inanimate use which, when used at effective concentrations are relatively non-irritant and which are effective against *Pseudomonas aeruginosa* to a degree comparable with their effects against most other pathogens.

It is well know that antiseptic and disinfectant fluids based on bactericidal phenol derivatives have satisfactory bacterial properties against the majority of pathogenic bacteria at substantially lower concentrations than are required to be effective against *Ps. aeruginosa*.

We have made the surprising discovery that antiseptic and disinfectant formulations based on bactericidal phenol derivatives are rendered much more effective against *Ps. aeurginosa* by the addition of certain proportions of stable organic sequestering agents (which are not themselves bactericidal). It is not, however, possible to obtain stable homogeneous germicidal fluids containing the stable organic sequestering agents merely by adding metallic salt solutions of the agents to an otherwise stable antiseptic or disinfectant fluid containing a bactericidal phenol derivative because the addition of such salt in sufficient quantity upsets the stability of the solution.

We have found, however, that stable homogeneous antiseptic and disinfectant fluids based on the bactericidal phenols can be prepared by the inclusion of triethanolamine or monoethanolamine in a quantity sufficient both to saponify the vegetable fat (where a soap is used in the formulation) and to provide an amount in slight excess of that required to neutralise the stable organic sequestering agents.

The antiseptic and disinfectant fluids of the present invention possess varying additional advantages.

For example, those formulations which contain soap do not form a scum on the sides of vessels in which they may be diluted with hard water.

Those formulated with sodium lauryl sulphate as an emulsifier can be made to give clear solutions when diluted with hard or soft water. Unlike fluids based on quaternary ammonium compounds, they are not, however, adversely affected when used in the presence of traces of soap.

According to the present invention there is provided an antiseptic and disinfectant composition comprising 0.5 to 5% by weight in volume of the composition of a bactericidal phenol derivative, 2 to 10% by weight in volume of the composition of a stable organic sequestering agent, triethanolamine or monoethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent, and a soap or emulsifying agent. There is also provided a disinfectant fluid comprising 0.5 to 5% w/v bactericidal phenol derivative, 2 to 10% w/v ethylenediaminetetra-acetic acid, 4 to 20% w/v triethanolamine or 1.7 to 8.4% w/v monoethanolamine, 1 to 10% sodium lauryl sulphate or the triethanolamine, or monoethanolamine salt of castor oil soap, 10 to 30% w/v alcoholic solvent and water to make 100%.

The alcoholic solvent is preferably indus-

trial methylated spirit.

The invention further provides a method for the preparation of a disinfectant composition comprising dissolving a bactericidal phenol derivative in an alcoholic solvent and adding thereto a solution formed by treating a stable organic sequestering agent with water and monoethanolamine or triethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent and a solution formed by neutralising a free fatty acid of a soap with the stoichiometric amount of triethanolamine or monoethanolamine, adding water and stirring until a clear solution is obtained.

The invention also provides a method for the preparation of a disinfectant composition comprising dissolving a bactericidal phenol derivative in an alcoholic solvent and adding thereto an emulsifying agent and a solution formed by treating a stable organic sequestering agent with water and monoethanolamine or triethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent, adding water and stirring until a clear solution is obtained.

The preferred organic sequestering agent is ethylenediaminetetra-acetic acid employed in amount of 8% by weight in volume of the composition. 1% by weight in volume of the composition of the bactericidal phenol derivative may conveniently be employed.

Bactericidal phenol derivatives which are suitable for this invention may be selected from the compounds usually used in antiseptics and disinfectants which have one phenolic hydroxyl group attached to the aromatic ring and which may have one or more other substituents in the ring such as methyl, ethyl, phenyl, benzyl or halogen. In addition, phenolic derivatives in which two aromatic rings, both of which have a phenolic hydroxy group attached, are joined together by a methylene bridge or a sulphur atom and which may contain one or more methyl, ethyl or halogen substituents may be used. Mixtures of isomers, technically produced, such as dichloro-3-methyl-5-ethylphenol or individual phenols such as 2-benzyl-4-chlorophenol and 4-chloro-3:5-dimethylphenol also may be used.

Emulsifying agents which may be used for the disinfectant fluids of this invention may be triethanolamine or monoethanolamine salts of the fatty acids from castor oil or sodium lauryl sulphate or detergent materials obtained by sulphating olefinic compounds.

The preferred stable organic sequestering agent for this invention is ethylenediaminetetra-acetic acid, but other alkylene polyamino polycarboxylic acids with sufficiently strong sequestering properties are satisfactory and the following materials can all be successfully used in the invention:—Diaminocyclohexanetetra-acetic acid, *N*-hydroxyethylethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid; 1:2-propylenediaminetetra-acetic acid.

The pH of those antiseptic and disinfectant fluids which include soap is preferably adjusted to pH 9. The pH of the other fluids is preferably adjusted to between 7 and 9.

The antiseptic and disinfectant compositions of this invention may be prepared as follows:—

Method 1—If a soap is incorporated

The soap is prepared by using the stoichiometric amount of triethanolamine or monoethanolamine to neutralise the free fatty acid of the soap to be used. The ingredients, in the correct proportions, are stirred together with an amount of water at least equal to but not exceeding twice the weight of the ingredients until a clear solution is obtained.

The ethylenediaminetetra-acetic acid or other sequestering agent is treated with the correct amount of triethanolamine or monoethanolamine by vigorously stirring it with approximately twice its weight of water and pouring the alkali in slowly. The best results are obtained, when using ethylenediaminetetra-acetic acid as the sequestering agent, if sufficient alkali to be equivalent to all four acid groupings is used.

The phenolic material is dissolved in industrial methylated spirit and the above two solutions added. Water is added to give the total volume and the whole is stirred until a clear solution is obtained.

Method 2—If other emulsifying agents are used

The ethylenediaminetetra-acetic acid, or other sequestering agent, is treated with the correct amount of triethanolamine or monoethanolamine by vigorously stirring it with approximately twice its weight of water and pouring the alkali in slowly. The best results are obtained, when using ethylenediamine tetraacetic acid as the sequestering agent, if sufficient alkali to be equivalent to all four acid groupings is used.

The phenolic material is dissolved in industrial methylated spirit and the ethylenediaminetetra-acetic acid solution and the emulsifier are added. Water is added to give the total volume and the whole is stirred until a clear solution is obtained.

Following is a description by way of example of methods of carrying the invention into effect.

EXAMPLE 1

2-Benzyl-4-chlorophenol	1.0% w/v
Ethylenediaminetetra-acetic acid	8.0% w/v
Castor oil fatty acid	3.3% v/v
Monoethanolamine	7.2% w/v
Industrial methylated spirit	32.0% v/v
Water to make	100%

These materials were mixed according to Method 1 given above and produced a clear, stable foaming liquid, which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing *Salmonella typhosa* and *Ps. aeurginosa* in 10 but not 5 minutes at 20° C. were 1 in 565 and 380, respectively. By contrast, a fluid made without the ethylenediaminetetra-acetic acid and the corresponding monoethanolamine only killed *Ps. aeruginosa* at a dilution of 1 in 1.5.

EXAMPLE 2

Dichloro-*m*-xylenol	1.0% w/v
Ethylenediaminetetra-acetic acid	8.0% w/v
Castor oil fatty acid	2.3% v/v
Triethanolamine	17.3% w/v
Terpineol	2.0% v/v
Industrial methylated spirit	35.0% v/v
Water to make	100%

The materials were mixed according to Method 1 except that the terpineol (added to prevent the dichloro *m*-xylenol from crystallising out from working strength dilutions) as well as the phenolic material was dissolved initially in the industrial methylated spirit. A clear stable foaming liquid was obtained, which was clear at all temperatures from 0° C. to its boiling point. The highest dilutions killing *S. typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 20° C. were 1 in 225 and 255, respectively. By contrast, a fluid made without the ethylenediaminetetra-acetic acid and the corresponding triethanolamine only killed *Ps. aeurginosa* at a dilution of 1 in 6.

EXAMPLE 3

2-Benzyl-4-chlorophenol	1.0% w/v
Sodium laurel sulphate	2.0% w/v
Ethylenediaminetetra-acetic acid	8.0% w/v
Triethanolamine	16.3% w/v
Industrial methylated spirit	21.0% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable foaming liquid, which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing *S typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 20° C. were 1 in 570 and 340, respectively. By contrast, a fluid made without the ethylenediaminetetraacetic acid and triethanolamine only killed *Ps. aeruginosa* at a dilution of 1 in 3.

EXAMPLE 4

2-Benzyl-4-chlorophenol	1.0% w/v
"Teepol" (Registered Trade Mark)	10.0% v/v
Ethylenediaminetetra-acetic acid	8.0% w/v
Triethanolamine	16.3% w/v
Industrial methylated spirit	21.0% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable foaming liquid, which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing *S. typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 20° C. were 1 in 340 and 275, respectively. By contrast, a fluid made without the ethylenediaminetetra-acetic acid and triethanolamine only killed *Ps. aeruginosa* at a dilution of 1 in 1.5.

EXAMPLE 5

"Cresantol 16" (Registered Trade Mark)	1% w/v
Ethylenediaminetetra-acetic acid	8% w/v
"Teepol" (Registered Trade Mark)	10% v/v
Triethanolamine	16.3% w/v
Industrial methylated spirit	25% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable foaming liquid, which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing *S. typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 20° C. were 1 in 170 and 90, respectively. By contrast, a fluid made without the ethylenediaminetetra-acetic acid and triethanolamine only killed *Ps. aeruginosa* at a dilution of 1 in 9.

EXAMPLE 6

Thio bis (2-hydroxy-3-methyl benzene)	1% w/v
Ethylenediaminetetra-acetic acid	8% w/v
Triethanolamine	17.7% w/v
Castor oil fatty acid	3.3% v/v
Industrial methylated spirit	25% v/v
Water to make	100%

The materials were mixed according to Method 1 and produced a clear, stable foaming liquid, which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing *S. typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 200° C. were 1 in 250 and 240, respectively. By contrast, a fluid made without the ethylenediaminetetra-acetic acid and the corresponding triethanolamine only killed *Ps. aeruginosa* at a dilution of 1 in 1.5.

EXAMPLE 7

2-Benzyl-4-chlorophenol	1% w/v
Diamino*cyclo*hexanetetra-acetic acid	8% w/v
Triethanolamine	13.8% w/v
Sodium lauryl sulpnate	3% w/v
Industrial methylated spirit	25% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable, foaming liquid, which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing *S. typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 20° C. were 1 in 570 and 160, respectively. By contrast, a fluid made without the diamino*cyclo*hexanetetra-acetic acid and triethanolamine only killed *Ps. aeruginosa* at dilution of 1 in 1.5.

EXAMPLE 8

2-Benzyl-4-chlorophenol	1% w/v
N-Hydroxyethylethylenediamine triacetic acid as sodium salt	8% w/v
Industrial methylated spirit	32% v/v
Castor oil fatty acid	2.7% v/v
Monoethanolamine	0.5% w/v
Water to make	100%

The materials were mixed according to Method 1 except that the sodium salt of *N*-hydroxyethylethylenediaminetri - acetic acid was used. The fluid given in the formula above produced a clear, stable, foaming liquid, which was clear at all temperatures from 0° C. to its boiling point. The highest dilutions killing *S. typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 20° C. were 1 in 440 and 120, respectively. By contrast, a fluid made without the *N*-hydroxyethylethylenediaminetriacetic acid only killed *Ps. aeruginosa* at a dilution of 1 in 1.5.

EXAMPLE 9

2-Benzyl-4-chlorophenol	1% w/v
1:2-Propylenediaminetetra-acetic acid	8% w/v
Triethanolamine	15.6% w/v
Sodium lauryl sulphate	3% w/v
Industrial methylated spirit	29% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable, foaming liquid, which was clear at all temperatures from 0° C. to its boiling point. The highest dilutions killing *S. typhosa* and *Ps. aeruginosa* in 10 but not 5 minutes at 20° C. were 1 in 700 and 180, respectively. By contrast, a fluid made without the 1:2-propylenediaminetetra-acetic acid and triethanolamine only killed *Ps. aeruginosa* at a dilution of 1 in 1.7.

WHAT WE CLAIM IS:—

1. An antiseptic and disinfectant composition comprising 0.5 to 5% by weight in volume of the composition of a bactericidal phenol derivative, 2 to 10% by weight in volume of the composition of a stable organic sequestering agent, triethanolamine or monoethanolamine at least in an amount in excess of that required to neutralise the organic sequestering agent, and a soap or emulsifying agent.

2. A composition as claimed in claim 1, wherein the bactericidal phenol derivative is 2-benzyl-4-chlorophenol or dichloro-*m*-xylenol.

3. A composition as claimed in claim 1 or claim 2, wherein the sequestering agent is ethylenediaminetetra-acetic acid, diaminocyclohexanetetra-acetic acid, *N*-hydroxyethylethylenediaminetri-acetic acid or 1:2-propylenediaminetetra-acetic acid.

4. A composition as claimed in any one of the preceding claims, wherein the emulsifying agent is the triethanolamine or monoethanolamine salt of the fatty acids from castor oil, or sodium lauryl sulphate, or detergent materials obtained by sulphating olefinic compounds.

5. A composition according to claim 1, comprising 0.5 to 5% w/v bactericidal phenol derivative, 2 to 10% w/v ethylenediaminetetra-acetic acid, 4 to 20% w/v triethanolamine or 1.7 to 8.4% w/v monoethanolamine, 1 to 10% sodium lauryl sulphate or the triethanolamine or monoethanolamine salt of castor oil soap, 10 to 30% w/v alcoholic solvent and water to make 100%.

6. A composition as claimed in claim 5, wherein the alcoholic solvent is industrial methylated spirit.

7. A composition as claimed in any one of the preceding claims, wherein the organic sequestering agent is ethylenediaminetetra-acetic acid employed in an amount of 8% by weight in volume of the composition.

8. A composition as claimed in any one of the preceding claims, wherein the bactericidal phenol derivative is employed in an amount of 1% by weight in volume.

9. A method for the preparation of a disinfectant composition comprising dissolving a bactericidal phenol derivative in an alcoholic solvent and adding thereto a solution formed by treating a stable organic sequestering agent with water and monoethanolamine or triethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent and a solution formed by neutralising a free fatty acid of a soap with the stoichiometric amount of triethanolamine or monoethanolamine, adding water and stirring until a clear solution is obtained.

10. A method as claimed in claim 9, wherein the pH of the composition is adjusted to 9.

11. A method for the preparation of a disinfectant composition comprising dissolving a bactericidal phenol derivative in an alcoholic solvent and adding thereto an emulsifying agent and a solution formed by treating a stable organic sequestering agent with water and monoethanolamine or triethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent, adding water and stirring until a clear solution is obtained.

12. A method as claimed in claim 11, wherein the pH of the composition is adjusted to between 7 and 9.

13. A method for the preparation of an antiseptic and disinfectant composition substantially as described with reference to the specific Examples hereinbefore set forth.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

Improvements in or relating to Antiseptics and Disinfectants

We, RECKITT & SONS LIMITED, a British Company, of Dansom Lane, Hull, Yorkshire, SYDNEY NORMAN HERBERT STOTHART, a British Subject, of 51, Allderidge Avenue, Hull, Yorkshire, and GEOFFREY CHARLES BEECROFT, a British Subject, of 15, Cayton Road, Hull Yorkshire, do hereby declare this invention to be described in the following statement:—

This invention is for improvements in or relating to antiseptics and disinfectants.

It is an object of the present invention to provide antiseptic and disinfectant fluids for personal use and other purposes which, when used at effective concentrations are relatively non-irritant and which are effective against Pseudomonas aeruginosa to a degree comparable with their effects against most other pathogens.

It is well known that antiseptic and disinfectant fluids based on bactericidal phenol derivatives have satisfactory bactericidal properties against the majority of pathogenic bacteria at substantially lower concentrations

than are required to be effective against Ps. aeruginosa.

We have made the surprising discovery that antiseptic and disinfectant formulations based on bactericidal phenol derivatives are rendered much more effective against Ps. aeruginosa by the addition of certain proportions of stable organic sequestering agents (which are not themselves bactericidal). It is not, however, possible to obtain stable homogeneous germicidal fluids containing the stable organic sequestering agents merely by adding metallic salt solutions of the agents to an otherwise stable antiseptic or disinfectant fluid containing a bactericidal phenol derivative because the addition of such salt in sufficient quantity upsets the stability of the solution.

We have found, however, that stable homogeneous antiseptic and disinfectant fluids based on the bactericidal phenols can be prepared by the inclusion of triethanolamine or monoethanolamine in a quantity sufficient both to saponify the vegetable fat (where a soap is used in the formulation) to provide an amount in slight excess of that required to neutralise the stable organic sequestering agents.

The antiseptic and disinfectant fluids of the present invention possess varying additional advantages.

For example, those formulations which contain soap do not form a scum on the sides of vessels in which they may be diluted with hard water.

Those formulated with sodium lauryl sulphate as an emulsifier can be made to give clear solutions when diluted with hard or soft water. Unlike fluids based on quaternary ammonium compounds, they are not, however, adversely affected when used in the presence of traces of soap.

According to the present invention there is provided a disinfectant composition comprising 0.5 to 5% by weight in volume of the composition of a bactericidal phenol derivative, 2 to 10% by weight in volume of the composition of a stable organic sequestering agent, triethanolamine or monoethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent, and a soap or emulsifying agent.

There is also provided a disinfectant fluid comprising 0.5 to 5% w/v bactericidal phenol derivative, 2 to 10% w/v ethylene diamine tetraacetic acid, 4 to 20% w/v triethanolamine or 1.7 to 8.4% w/v monoethanolamine, 1 to 10% sodium lauryl sulphate or the triethanolamine, or monoethanolamine salt of castor oil soap, 10 to 30% w/v alcoholic solvent and water to make 100%.

The alcoholic solvent is preferably industrial methylated spirit.

The invention further provides a method for the preparation of a disinfectant composition comprising dissolving a bactericidal phenol derivative in an alcoholic solvent and adding thereto a solution formed by treating a stable organic sequestering agent with water and monoethanolamine or triethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent and a solution formed by neutralising a free fatty acid of a soap with the stoichiometric amount of triethanolamine or monoethanolamine, adding water and stirring until a clear solution is obtained.

The invention also provides a method for the preparation of a disinfectant compcsition comprising dissolving a bactericidal phenol der.vative in an alcoholic solvent and adding thereto an emulsifying agent and a solution formed by treating a stable organic sequestering agent with water and monoethanolamine or triethanolamine at least in amount in excess of that required to neutralise the organic sequestering agent, adding water and stirring until a clear solution is obtained.

The preferred organic sequestering agent is ethylene diamine tetraacetic acd employed in amount of 8% by weight in volume of the composition. 1% by weight in volume of the composition of the bactericidal phenol derivative may conveniently be employed.

Bactericidal phenol derivatives which are suitable for this invention may be selected from the compounds usually used in antiseptics and disinfectants which have one phenolic hydroxyl group attached to the aromatic ring and which may have one or more other substituents in the ring such as methyl, ethyl, phenyl, benzyl or halogen. In addition, phenolic derivatives in which two aromatic rings, both of which have a phenolic hydroxy group attached are joined together by a methylene bridge or a sulphur atom and which may contain one or more methyl, ethyl or halogen substituents may be used. Mixtures of isomers, technically produced, such as dichlor 3-methyl 5-ethyl phenol or of individual phenols such as *o*-benzyl-p-chlor phenol and p-chlor sym, m-xylenol also may be used.

Emulsifying agents which may be used for the disinfectant fluids of this invention may be triethanolamine or monoethanolamine salts of the fatty acids from castor oil or sodium lauryl sulphate or detergent materials obtained by sulphating olefinic compounds.

The preferred stable organic sequestering agent for this invention is ethylene diamine tetraacetic acid in the forms of its triethanolamine or mono-ethanolamine salt but other alkylene amino polyacids with sufficiently strong sequestering properties are satisfactory and the following materials can all be successfully used in the invention:—diamino cyclohexone tetraacetic acid, N-hydroxy ethyl ethylene diamine triacetic acid, diethylene triamine pentacetic acid, 1,2-propylene di-

amine tetraacetic acid.

The pH of those antiseptic and disinfectant fluids which include soap is preferably adjusted to pH 9. The pH of the other fluids is preferably adjusted to between 7 and 9.

The antiseptic and disinfectant compositions of this invention may be prepared as follows:—

Method 1—If a soap is incorporated

The soap is prepared by using the stoichiometric amount of triethanolamine or monoethanolamine to neutralise the free fatty acid of the soap to be used. The ingredients, in the correct proportions, are stirred together with an amount of water at least equal to but not exceeding twice the weight of the ingredients until a clear solution is obtained.

The ethylene diamine tetraacetic acid or other sequestering agent is treated with the correct amount of triethanolamine or monoethanolamine by vigorously stirring it with approximately twice its weight of water and pouring the alkali in slowly. The best results are obtained, when using ethylene diamine tetraacetic acid as sequestering agent, if sufficient alkali to be equivalent to all four acid groupings is used.

The phenolic material is dissolved in industrial methylated spirit and the above two solutions added. Water is added to give the total volume and the whole is stirred until a clear solution is obtained.

Method 2—If other emulsifying agents are used

The ethylene diamine tetraacetic acid, or other sequestering agent, is treated with the correct amount of triethanolamine or monoethanolamine by vigorously stirring it with approximately twice its weight of water and pouring the alkali in slowly. The best results are obtained, when using ethylene diamine tetraacetic acid as the sequestering agent, if sufficient alkali to be equivalent to all four acid groupings is used.

The phenolic material is dissolved in industrial methylated spirit and the ethylene diamine tetraacetic acid solution and the emulfier are added. Water is added to give the total volume and the whole is stirred until a clear solution is obtained.

Following is a description by way of example of methods of carrying the invention into effect.

EXAMPLE 1

o-Benzyl *p*-chlor phenol	1.0% w/v
Ethylene diamine tetraacetic acid	8.0% w/v
Castor oil fatty acid	3.3% v/v
Monoethanolamine	7.2% w/v
Industrial methylated spirit	32.0% v/v
Water to make	100%

These materials were mixed according to Method 1 given above and produced a clear, stable foaming liquid which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing Salmonella typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 565 and 380 respectively. By contrast, a fluid made without the ethylene diamine tetraacetic acid and the corresponding monoethanolamine only killed Ps. aeruginosa at a dilution of 1 in 1.5.

EXAMPLE 2

Dichlor *m*-xylenol	1.0% w/v
Ethylene diamine tetraacetic acid	8.0% w/v
Castor oil fatty acid	2.3% v/v
Triethanolamine	17.3% w/v
Terpineol	2.0% v/v
Industiral methylated spirit	35.0% v/v
Water to make	100%

The materials were mixed according to Method 1 except that the terpineol (added to prevent the dichlor *m*-xylenol from crystallising out from working strength dilutions) as well as the phenolic material was dissolved initially in the industrial methylated spirit. A clear stable foaming liquid was obtained which was clear at all temperatures from 0° C. to its boiling point. The highest dilutions killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 225 and 255 respectively. By contrast, a fluid made without the ethylene diamine tetraacetic acid and the corresponding triethanolamine only killed Ps. aeruginosa at a dilution of 1 in 6.

EXAMPLE 3

o-Benzyl-*p*-chlor phenol	1.0% w/v
Sodium lauryl sulphate	2.0% w/v
Ethylene diamine tetraacetic acid	8.0% w/v
Triethanolamine	16.3% w/v
Industrial methylated spirit	21.0% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable foaming liquid which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 570 and 340 respectively. By contrast, a fluid made without the ethylene diamine tetraacetic acid and triethanolamine only killed Ps aeruginosa at a dilution of 1 in 3.

EXAMPLE 4

o-Benzyl *p*-chlor phenol	1.0% w/v
"Teepol" (Registered Trade Mark)	10.0% v/v
Ethylene diamine tetraacetic acid	8.0% w/v
Treithanolamine	16.3% w/v
Industrial Methylated spirit	21.0% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable foaming liquid which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 340 and 275 respectively. By contrast, a fluid made without the ethylene diamine tetraacetic acid and triethanolamine only killed Ps aeruginosa at a dilution of 1 in 1.5.

EXAMPLE 5

"Cresantol 16" (Registered Trade Mark)	1% w/v
Ethylene diamine tetraacetic acid	8% w/v
"Teepol" (Registered Trade Mark)	10% v/v
Triethanolamine	16.3% w/v
Industrial methylated spirit	25% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable foaming liquid which was clear at all temperatures from 0° C. to boiling point. The highest dilution killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 170 and 90 respectively. By contrast, a fluid made without the ethylene diamine tetraacetic acid and triethanolamine only killed Ps aeruginosa at a dilution of 1 in 9.

EXAMPLE 6

Di *o*-cresol sulphide	1% w/v
Ethylene diamine tetraacetic acid	8% w/v
Triethanolamine	17.7% w/v
Castor oil fatty acid	3.3% v/v
Industrial methylated spirit	25% v/v
Water to make	100%

The materials were mixed according to Method 1 and produced a clear stable foaming liquid which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 250 and 240 respectively. By contrast, a fluid made without the ethylene diamine tetraacetic acid and the corresponding triethanolamine only killed Ps. aeruginosa at a dilution of 1 in 1.5.

EXAMPLE 7

o-Benzyl *p*-chlor phenol	1% w/v
Diamino cyclo-hexane tetraacetic acid	8% w/v
Triethanolamine	13.8% w/v
Sodium lauryl sulphate	3% w/v
Industrial methylated spirit	25% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear stable foaming liquid which was clear at all temperatures from 0° C. to boiling point. The highest dilutions killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 570 and 160 respectively. By contrast, a fluid made without the diamino cyclohexane tetraacetic acid and triethanolamine only killed Ps. aeruginosa at dilution of 1 in 1.5.

EXAMPLE 8

o-Benzyl *p*-chlor phenol	1% w/v
N-Hydroxy ethyl ethylene diamine triacetic acid as sodium salt	8% w/v
Industrial methylated spirit	32% v/v
Castor oil fatty acid	2.7% v/v
Monoethanolamine	0.5% w/v
Water to make	100%

The materials were mixed according to Method 1 except that the sodium salt of N-hydroxy ethyl ethylene diamine triacetic acid was used. The fluid given in the formula above produced a clear stable, foaming liquid which was clear at all temperatures from 0° C. to its boiling point. The highest dilutions killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 404 and 120 respectively. By contrast, a fluid made without the N-hydroxyethyl ethylene diamine triacetic acid only killed Ps. aeruginosa at a dilution of 1 in 1.5.

EXAMPLE 9

o-Benzyl *p*-chlor phenol	1% w/v
1,2-Propylene diamine tetraacetic acid	8% w/v
Triethanolamine	15.6% w/v
Sodium lauryl sulphate	3% w/v
Industrial methylated spirit	29% v/v
Water to make	100%

The materials were mixed according to Method 2 and produced a clear, stable, foaming liquid which was clear at all temperatures from 0° C. to its boiling point. The highest dilutions killing S. typhosa and Ps. aeruginosa in 10 but not 5 minutes were 1 in 700 and 180 respectively. By contrast, a fluid made without the 1,2-propylene diamine tetraacetic acid and triethanolamine only killed Ps. aeruginosa at a dilution of 1 in 1.7.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

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(71) Applicants
Bristol-Myers Company, 345 Park Avenue, New York 10154, United States of America
(72) Inventors
Chung Teck Shin
Milton S. Slade
Ara Nersesian
(74) Agents
Carpmaels & Ransford, 43 Bloomsbury Square, London, WC1A 2RA

(54) **Antiperspirant composition containing aluminum chlorohydrate, aluminum chloride and an aluminum zirconium polychlorohydrate complex**

(57) An antiperspirant composition buffered to a pH in the range of from about 2.5 to about 4.5 having incorporated therein as active ingredients a mixture of aluminum chlorohydrate, aluminum chloride and an aluminum zirconium polychlorohydrate complex; an additionally added buffering agent, preferably glycine, may be incorporated in the composition.

GB 2 091 099 A

SPECIFICATION

Antiperspirant composition containing aluminum chlorohydrate, aluminum chloride and an aluminum zirconium polychlorohydrate complex, and method of use

This invention relates to antiperspirant compositions. More particularly, it concerns antiperspirant compositions having incorporated therein aluminum chlorohydrate, aluminum chloride, an aluminum zirconium polychlorohydrate complex and a buffering agent e.g. glycine.

Aluminum chlorhydrate (ACH) has been known for many years to be an effective and safe antiperspirant. Nevertheless, there is room for improvement, and the search to find more effective antiperspirant materials is constantly going on. It has also been known in the art for sometime that aluminum chloride and zirconium salts provide exceptionally effective antiperspirants. However, solutions of aluminum chloride hexahydrate and zirconium oxy- or hydroxychloride are very acidic and therefore, they are not widely used alone because of their irritation potential and high fabric damage. Therefore, various efforts have been centered on raising the pH to 3 to 4 by using less acidic aluminum salts and incorporating organic nitrogen containing compounds.

Daley (U.S. Patents 2,814,584 and 2,814,585) and Grad (U.S. Patent 2,854,382) showed that when zirconium oxy- or zirconium hydroxychloride are buffered with ACH and glycine, the antiperspirant efficacy is greater than an ACH system alone. Since then, the combination of aluminum chlorohydrate, zirconium hydroxychloride and glycine has been used widely as a most effective antiperspirant active system.

Luedders et al in U.S. Patent 3,792,068 suggest a process for preparing an antiperspirant which comprises spray drying a solution containing, for example, ACH, zirconyl hydroxychloride and glycine. It is claimed that this combination has superior characteristics not possessed when the components are dried separately and combined by simple physical mixing.

The British patent to Shin et al 1,347,950 discloses the use of a combination of ACH and aluminum chloride as an effective antiperspirant material. This combination was found to be particularly useful in an aerosol composition. However, as in the case with other antiperspirant materials known in the prior art, it still left room for improvement.

Other antiperspirant systems containing aluminum and zirconium salts have been reported, for example, Beekman (U.S. Patent 2,906,668), Rubino (U.S. Patents 3,979,510; 3,981,896 and 4,017,599), Siegel et al (U.S. Patent 3,407,254), Mecca (U.S. Patent 3,970,748), Shelton (U.S. Patent 4,202,879), etc. The antiperspirant activity of all these salts in these patents has not been clearly claimed as having superiority over systems containing zirconium hydroxychloride, ACH and glycine.

Although aluminum chloride, aluminum chlorohydrate, zirconyl hydroxychloride and certain aluminum zirconium chlorohydrate complexes, individually have been suggested for use as antiperspirant materials in the prior art, and the combination of aluminum chloride and aluminum chlorohydrate on the one hand, and the combination of aluminum chlorohydrate and zirconyl hydroxychloride on the other hand, have also been suggested for use as an active antiperspirant, it has been unexpectedly found that a combination of aluminum chloride, aluminum chlorohydrate, and an aluminum zirconium polychlorohydrate complex as defined more particularly below acts synergistically and at the same level of concentration of actives shows a higher degree of antiperspirant activity than would be expected from the level of activity of the individual ingredients or certain combination of ingredients which are shown in the prior art. In combination with a buffering agent e.g. glycine, these materials provide a high performance antiperspirant having a low potential for skin irritation and/or fabric damage.

It is accordingly an object of the present invention to provide highly effective antiperspirant compositions.

It is also an object of this invention to provide a process for inhibiting perspiration on the skin of individuals by application to the skin area the aforesaid antiperspirant compositions.

Other and more detailed objects of this invention will be apparent from the following description and claims.

In the following description, unless otherwise specified, the percentages are expressed as percentages by weight based on the total weight of the composition.

The aluminum chloride that is incorporated in the compositions of the present invention may be aluminum chloride hydrated to various degrees. However, aluminum chloride hexahydrate ($AlCl_3.6H_2O$) has been found to be most effective and is therefore preferred for the purposes of the present invention.

The quantity of aluminum chloride that may be incorporated in the present composition may vary somewhat. Generally, the aluminum chloride will be incorporated in these compositions at a level of between about 0.5% and about 6% by weight on an anhydrous basis based on the total weight of the composition. As the hexahydrate ($AlCl_3.6H_2O$) it will be incorporated at a concentration of from about 0.9% to about 11% by weight based on the total weight of the composition with the preferred range being from about 2% to about 6% on the same basis.

The aluminum chloride hexahydrate will usually be incorporated in the present composition as a 50% aqueous solution. When employed in this form, from about 1.8% to about 22% by weight of this composition based on the total weight of the composition will be used.

The aluminum chlorohydrate (sometimes referred to as aluminum chlorhydroxide) may also be incorporated in the composition of this invention in varying amounts. Usually, this will be used at a level in the range of from about 1% to about 15% by weight on an anhydrous basis based on the total weight of

the composition with the preferred level falling in the range of from about 2% to about 10% by weight on the same weight basis. Aluminum chlorohydrate is also supplied as a 50% aqueous solution. When employed in this form, it will be used at a concentration of from 2.6% to about 38% by weight based on the total weight of the composition.

The ACH and aluminum chloride may be added to this composition in whole or in part as a powdered mixture as described in the British patent to Shin et al 1,347,950. This may be prepared by drying an aqueous solution of aluminum chloride hexahydrate and ACH using conventional drying techniques such as oven drying, vacuum oven drying, spray drying or freeze drying. These compositions are characterized by the fact that the molar ratio of aluminum to chloride will fall within the range of from about 0.78:1 to about 1.95:1 with the preferred range being about 1.2:1 to about 1.5:1. When the molar ratio of aluminum to chloride is less than 1, the addition of larger amounts of buffering agent e.g. glycine may be necessary to reduce irritation potential and fabric damage.

The aluminum zirconium polychlorohydrate complexes that may be incorporated in the composition of the present invention may be described by the general formula:

(I) $Al_xZr(OH)_yCl_{2-n}H_2NCH_2COOH.mH_2O$

wherein:

(a) x is a number from 2 to 10;
(b) Z is a number from 3 to 8;
(c) y equals $(3x + 4) - Z$;
(d) the sum of $y + Z$ is a number from 10 to 34;
(e) m is a number from 0 to 12;
(f) n is a number from 0 to 3

y ordinarily will have a value of from about 5 to about 29.

As will be clear from Formula I, the glycine may be bound in the complex or it may be absent. The presence or absence of the glycine in the complex will determine the amount of unbound glycine or other buffer that may be incorporated in the composition to increase the pH to a level of from about 2.5 to about 4.5 or the preferred pH of from about 2.8 to about 3.8.

A number of aluminum zirconium polychlorohydrate complexes are known in the prior art which are useful for the present purposes. By way of example, the following may be mentioned along with their empirical formulas: aluminum zirconium tetrachlorohydrate ($Al_2Zr(OH)_{12}Cl_4$); aluminum zirconium tetrachlorohydrate glycine (Wickenol #E-369) ($Al_2Zr(OH)_{12}Cl_4 . NH_2CH_2COOH$); aluminum zirconium trichlorohydrate ($Al_2Zr(OH)_{11}Cl_5$; aluminum zirconium trichlorohydrate glycine ($Al_2Zr(OH)_{11}Cl_5 . NH_2CH_2COOH$); aluminum zirconium pentachlorohydrate ($Al_{10}Zr(OH)_{29}Cl_5$); aluminum zirconium pentachlorohydrate glycine ($Al_{10}Zr(OH)_{29}Cl_5 . NH_2CH_2COOH$); aluminum zirconium octachlorohydrate ($Al_2Zr(OH)_{13}Cl_6$); aluminum zirconium octachlorohydrate glycine ($Al_2Zr(OH)_{14}Cl_6 . NH_2CH_2COOH$).

The aluminum zirconium polychlorohydrate complex can be mixed individually with the ACH and $AlCl_3 . 6H_2O$ in solution or powder form or in various combinations thereof.

The OTC Panel on antiperspirants of the Food and Drug Administration has adopted certain nomenclature and specifications for various aluminum zirconium polychlorohydrates that are useful in the present invention. These are set out in Table A below:

Table A

Panel Adopted Nomenclature	*Metal-Halide Ratio Range*	*Al/Zr Ratio Range*
Aluminum zirconium trichlorohydrate	2.1 down to but not including 1.5:1	2.0 up to but not including 6.0:1
Aluminum zirconium tetrachlorohydrate	1.5 down to and including 0.9:1	2.0 up to but not including 6.0:1
Aluminum zirconium pentachlorohydrate	2.1 down to but not including 1.5:1	6.0 up to and including 10.0:1
Aluminum zirconium octachlorohydrate	1.5 down to and including 0.9:1	6.0 up to and including 10.0:1

A number of the aluminum zirconium polychlorohydrate complexes that are useful in the present invention are available commerically. Reheis Chemical Company promotes a series of materials under the general trademark REZAL™. The following Table B describes a number of these products together with their specifications:

Table I

1 REZAL 36G Aluminum zirconium tetrachlorohydrex Gly (soln.)
2 REZAL 36 Aluminum zirconium trichlorohydrate (pdr.)
3 REZAL 67 Aluminum zirconium pentachlorohydrate (soln.)
4 REZAL 67 Aluminum zirconium pentachlorohydrate (pdr.)

	1	2	3	4
Approx. Al/Zr ratio	3.6:1	3.6:1	6.7:1	6.7:1
Approx. metal/Cl ratio	1.4:1	1.6:1	1.7:1	1.7:1
Concentration of solids	~35%	100%	~40%	100%
Aluminum (Al)	5.0%-5.7%	16.3%-17.7%	7.6%-8.4%	19.0%-21.0%
Zirconium (Zr)	4.4%-5.7%	13.8%-15.2%	3.7%-4.3%	9.2%-10.8%
Glycine	3.6%-4.7%	–	–	–
Chloride (Cl)	5.9%-6.7%	16.0%-19.0%	6.5%-7.2%	16.2%-18.0%
Iron (Fe)	NMT 50ppm	NMT 100ppm	NMT 50ppm	NMT 100ppm
Heavy metals (as Pb)	NMT 10ppm	NMT 20ppm	NMT 10ppm	NMT 20ppm
Particle size (thru 325 mesh)	–	>97% min.	–	>97% min.

Similar products are marketed by Wickhen Products, Inc. and the Comet Chemical Corporation.

The quantity of any aluminum zirconium polychlorohydrate complex that will be incorporated in the composition of the present invention may also vary somewhat. Usually, it will be used at a concentration level in the range of from about 5% to about 16% by weight on an anhydrous basis based on the total weight of the composition. In the preferred forms of this invention, the levels will be in the range of from about 8% to about 14% by weight on an anhydrous basis based on the total weight of the composition.

The aluminum zirconium polychlorohydrate complex of choice in the present invention is aluminum zirconium tetrachlorohydrate glycine complex. This is usually used at a level of from about 5% to about 16% by weight on an anhydrous basis based on the total weight of the composition, with the preferred level being in the range of from about 8% to about 14% based on the same weight basis. The aluminum zirconium tetrachlorohydrate glycine complex is supplied as a 35% aqueous solution. When employed in this form, it is usually incorporated in the present composition at a level in the range of from about 18% to about 60% by weight based on the total weight of the composition.

Glycine, the preferred buffering agent, is an important component of the present composition. This may be incorporated as free glycine or as part of the aluminum zirconium polychlorohydrate complex or as a combination of the both. In general, the total glycine incorporated in these compositions (i.e. as free glycine, complexed glycine or a combination of both) will fall in the range of from about 0.5% to about 5% by weight based on the total weight of the composition. The preferred range of total glycine, however, is from about 1.5% to about 3% on the same weight basis.

Other buffering or complexing agents besides glycine can also be used in this invention. For example, other amino acids or their salts (e.g. sodium glycinate, dihydroxy aluminum glycinate), urea, organic base containing nitrogen, metal hydroxide, carbonate, and oxide including alkaline and alkaline earth metal ($Mg(OH)_2$, Na_2CO_3, ZnO, etc.). These buffering agents can be used alone or in combination with glycine to give the composition a pH in the range of from 2.5 to 4.5 (preferably 2.8 to 3.8).

These complexing and buffering agents serve to reduce irritation potential and fabric damage. They also function to stabilize the antiperspirant system.

The compositions of the present invention may take a variety of dosage forms. Thus, they might be emulsion roll-on products or a clear hydro-alcoholic or aqueous roll-on products. Aqueous solutions of the aluminum chloride, ACH, aluminum zirconium polychlorohydrate complex and buffering agent e.g. glycine may be spray dried into an impalpable powder. This can be used as such or incorporated into sticks, suspensions, powders or roll-on products.

Although the compositions of the present invention may take a variety of forms, they appear very effective in systems that contain a relatively high water content. These may take the form of solution or emulsion in which the active ingredients (i.e. the aluminum chloride, ACH, aluminum zirconium polychlorohydrate complex and buffer) are contained in the aqueous phase. The aqueous emulsion systems are preferred since they give more organoleptically elegant compositions. These emulsion systems will usually be of the oil-in-water type in which the active ingredients will be contained in the continuous aqueous phase.

The quantity of water that may be contained in these compositions may vary somewhat. Usually, it will comprise from about 40% to about 80% by weight based on the total weight of the composition, the preferred range being from about 60% to about 75% on the same weight basis.

The emulsion type products of the present inven-

tion may also contain other ingredients that are commonly found in roll-on antiperspirant of the lotion or emulsion type. These will include such things as emollients, surfactants, sequestering agents, perfumes, coloring agents, etc. By way of illustrating the emollients that may be employed herein, mention may be made of fatty acid esters (isopropyl myristate, isopropyl palmitate); diesters of dicarboxylic acids (diisopropyl adipate), polyoxyalkylene glycol esters (polypropylene glycol 2000 monooleate); propylene glycol diesters of short chain fatty acids (C_6-C_{10}) (Neobee M-20); polyoxypropylene fatty ethers (Procetyl, Arlamol E, Witconol APS, Witconol APM, etc.), propoxylated monohydric alcohol M.W. 880-930 (Fluid AP), fatty alcohol (hexadecyl alcohol), silicons oils (dimethyl polysiloxane, 10-2000 centistokes), cyclomethicones (volatile silicone 7207 and 7158-Union Carbide), polyoxyethylene polyoxypropylene fatty ether (Procstyl AWS Modified, Witconol APES). Alone or mixtures of the above non-polar liquids are equally suitable for the purposes of this invention. Generally, the above emollients are organic oily liquids which are non-polar in character and have (a) a boiling point under atmospheric pressure not lower than about 120°C; (b) a specific gravity between about 0.7 and 1.6, preferably between 0.7 and 1.2.

The quantity of emollient employed will vary somewhat, the level usually being within the range of from about 1% to about 30% by weight based on the total weight of the composition. Preferably, this will fall in the range of from about 2% to about 15% on the same weight basis.

A variety of surfactants and combinations of surfactants are also useful in preparing the present lotion or emulsion type products. These include such materials as generally nonionic, cationic and amphoteric surfactants which can be used in antiperspirant emulsion systems. Examples are as follows:

I. *Nonionic Surfactants*

1. Polyoxyethylene fatty ethers – Brij 30, Brij 35, Brij 72, Brij 78, etc.

2. Polyoxypropylene polyoxyethylene fatty ethers – Procetyl AWS, Witconol APEM, Witconol APES, etc.

3. Polyoxyethylene alkyl phenyl ethers – Igepal CO 530, etc.

4. Polyoxyethylene sorbitan fatty acid esters – Tween 20, Tween 80, etc.

5. Sorbitan fatty acid esters – Span 60, Span 85, etc.

6. Lanolin ethers – Laneto 50, Solulan 98, etc.

7. Fatty alcohols and polyoxyethylene fatty ethers – Promulgen G, Polawax, etc.

II. *Cationic Surfactants*

N(Lauryl colamino formyl methyl)pyridinium chloride (Emcol E607L)

III. *Amphoteric Surfactants*

Coconut imidazoline (Monateric CA-35%)

IV. *Auxiliary Surfactants*

1. Glyceryl fatty acid esters – Glyceryl monostearate

2. Fatty acid amides – Witcamide 70 (Witco Chem. Co.)

3. Fatty alcohols – Stearyl alcohol

As in the case with the emollients, the quantity employed can vary somewhat. For the most part, this will be in the range of from about 1% to about 10% by weight on an anhydrous basis based on the total weight of the composition with the preferred range being from about 2% to about 6% on the same weight basis.

As indicated above, one of the popular antiperspirant systems employed in the prior art is an aluminum zirconium trichlorohydrate glycine complex. The present system has the following advantages over said popular system:

1. Low cost of goods. The above popular system is much more expensive than either $AlCl_3 \cdot 6H_2O$ or ACH.

2. Better emulsion stability and more ease to manufacture. Straight Al/Zr polychlorohydrate glycine systems are difficult to stabilize and to manufacture as emulsions.

3. Low fabric staining potential. Generally, straight Al/Zr polychlorohydrate glycine salts stain more than aluminum salts.

The following Examples are given to further illustrate the present invention. It is to be understood, however, that the invention is not limited thereto.

EXAMPLE 1
Formula 1908

Ingredients	*% by Wt.*
PPG-11 stearyl ether	2.25
Polyoxyethylene(2)stearyl ether	1.65
Polyoxyethylene(20)stearyl ether	0.60
Perfume	0.30
Disodium edetate, dihydrate	0.10
Water, deionized	35.40
Aluminum chlorhydroxide, 50%	18.00
Aluminum chloride hexahydrate solution, 50%	6.00
Aminoacetic acid (Glycine Crystal USP)	0.50
Aluminum zirconium tetrachlorohydrex-glycine solution, 35%	35.00
Color FD&C Blue #1 (0.1% Aq. Sol.)	0.20
	100.00

Appearance: Smooth, opaque lotion
Color: Pale blue
pH: 3.3 ± 0.3
Viscosity: #3 spindle at 20 RPM 15 seconds
Overnight viscosity: 500-1500 cps

Procedure:

1. In a suitable stainless steel kettle, melt together polyoxypropylene fatty alcohol ethers, polyoxyethylene(2)stearyl ether and polyoxyethylene(20)stearyl ether by heating to 140°F. Add the perfume and mix together just prior to Step 3.

2. In a separate stainless steel kettle, dissolve the disodium edetate in the water and heat to 140°F.

3. Slowly add the oil phase to the water phase (both at 140°F) using a Lightnin' mixer at slow agitation. Maintain the temperature of 140°F for 15 minutes.

4. At 140°F, slowly add to the batch, using slow agitation, a solution consisting of the aluminum

chlorhydroxide, aluminum chloride hexahydrate, glycine and aluminum zirconium tetrachlorohydrex-glycine solution which has been preheated to 120°F. Continue agitation and cool the batch to 125°F. Mix for 15 minutes, maintaining the batch temperature at 120°F-125°F.

5. Cool the batch to 105°F, add the dye solution and continue agitation and cooling.

6. When the batch temperature reaches 80°-85°F, stop agitation and adjust for water loss, if necessary.

EXAMPLE 2

The composition and procedure of Example 1 is followed except that in place of the PPG-11 stearyl ether, Arlamol ESP (PPG-15 stearyl ether) is employed.

EXAMPLE 3

Formula 1956

Following the procedure of Example 1, the following composition is prepared:

Ingredients	% *by Wt.*
PPG-11 stearyl ether	2.25
Polyoxyethylene(2)stearyl ether	1.65
Polyoxyethylene(20)stearyl ether	0.60
Perfume	0.32
Disodium edetate, dihydrate	0.10
Water, deionized	35.13
Butylated hydroxytoluene	0.05
Aluminum chlorhydroxide, 50%	18.00
Aluminum chloride hexahydrate solution, 50%	6.00
Aminoacetic acid (Glycine Crystal USP)	0.50
Aluminum zirconium tetrachlorohydrex-glycine solution, 35%	35.00
D&C Red #19 (0.1% Aq. Sol.)	0.08
D&C Yellow #10 (0.1% Aq. Sol.)	0.32
	100.00

Appearance: Smooth, opaque lotion
Color: Pink
pH: 3.3 ± 0.3
Viscosity: #3 spindle at 20 RPM 15 seconds
Overnight viscosity: 500-1500 cps

EXAMPLE 4

The composition and procedure of Example 3 is followed excepting that in place of the PPG-11 stearyl ether, Arlamol ESP (PPG-15 Stearyl Ether) is used.

EXAMPLE 5

The procedure of Example 1 is followed and the following composition is prepared:

Ingredients	% *by Wt.*
PPG-11 stearyl ether	2.25
Polyoxyethylene(2)stearyl ether	1.65
Polyoxyethylene(20)stearyl ether	0.60
Perfume	0.30
Disodium edetate, dihydrate	0.10
Water, deionized	31.40
Aluminum chlorhydroxide, 50%	12.00
Aluminum chloride hexahydrate solution, 50%	6.00
Aminoacetic acid (Glycine Crystal USP)	0.50
Aluminum zirconium tetrachlorohydrex-glycine solution, 35%	45.00
FD&C Blue #1 (0.1% Aq. Sol.)	0.20
	100.00

Appearance: Smooth, opaque lotion
Color: Pale blue
pH: 3.3 ± 0.3
Viscosity: #3 spindle at 20 RPM 15 seconds
Overnight viscosity: 500-1500 cps

EXAMPLE 6

The procedure and composition of Example 5 is followed excepting that in place of the PPG-11 stearyl ether, Arlamol ESP (PPG-15 Stearyl Ether) is employed.

EXAMPLE 7

Formula 1979

The procedure of Example 1 is followed and the following composition is prepared:

Ingredients	% *by Wt.*
PPG-11 stearyl ether	2.25
Polyoxyethylene(2)stearyl ether	1.65
Polyoxyethylene(20)stearyl ether	0.60
Perfume	0.30
Disodium edetate, dihydrate	0.10
Water, deionized	35.40
Aluminum chlorhydroxide, 50%	15.50
Aluminum chloride hexahydrate solution, 50%	8.00
Aminoacetic acid (Glycine Crystal USP)	1.00
Aluminum zirconium tetrachlorohydrex-glycine solution, 35%	35.00
FD&C Blue #1 (0.1% Aq. Sol.)	0.20
	100.00

Appearance: Smooth, opaque lotion
Color: Pale blue
pH: 3.3 ± 0.3
Viscosity: #3 spindle at 20 RPM 15 seconds
Overnight viscosity: 500-2000 cps

EXAMPLE 8

The composition and procedure of Example 7 is followed excepting that in place of the PPG-11 stearyl ether, Arlamol ESP (PPG-15 Stearyl Alcohol) is employed.

EXAMPLE 9
Formula 1991

The procedure of Example 1 is followed and the following composition is prepared:

Ingredients	*% by Wt.*
PPG-11 stearyl ether	2.25
Polyoxyethylene(2)stearyl ether	1.65
Polyoxyethylene(20)stearyl ether	0.60
Perfume	0.30
Disodium edetate, dihydrate	0.10
Water, deionized	31.40
Aluminum chlorhydroxide, 50%	10.00
Aluminum chloride hexahydrate solution, 50%	8.00
Aminoacetic acid (Glycine Crystal USP)	0.50
Aluminum zirconium tetrachlorohydrex - glycine solution, 35%	45.00
FD&C Blue #1 (0.1% Aq. Sol.)	0.20
	100.00

Appearance: Smooth, opaque lotion
Color: Pale blue
pH: 3.3 ± 0.3
Viscosity: #1 spindle at 20 RPM 15 seconds
Overnight viscosity: 500-1500 cps

EXAMPLE 10

The composition and procedure of Example 9 is followed excepting that in place of the PPG-11 stearyl ether, Arlamol ESP (PPG-15 Stearyl Ether) is employed.

EXAMPLE 11
Formula 1956

The procedure of Example 1 is followed and the following composition is prepared:

Ingredients	*% by Wt.*
PPG-11 stearyl ether	2.25
Polyoxyethylene(2)stearyl ether	1.65
Polyoxyethylene(20)stearyl ether	0.60
Perfume	0.30
Disodium edetate, dihydrate	0.10
Water, deionized	35.60
Aluminum chlorhydroxide, 50%	18.00
Aluminum chloride hexahydrate solution, 50%	6.00
Aminoacetic acid (Glycine Crystal USP)	0.50
Aluminum zirconium tetrachlorohydrex - glycine solution, 35%	35.00
	100.00

Appearance: Smooth, opaque lotion
Color: White
pH: 3.3 ± 0.3
Viscosity: #3 spindle at 20 RPM 15 seconds
Overnight viscosity: 500-1500 cps

EXAMPLE 12

The composition and procedure of Example 11 is followed excepting that in place of the PPG-11 stearyl ether, Arlamol ESP (PPG-15 Stearyl Ether) is employed.

EXAMPLE 13
Formula BA 1810-64

Aluminum zirconium trichlorohydrate 31 powder was employed. The number following the term "trichlorohydrate" in this and other Examples designates the Al/Zr molar ratio in the compound. Thus, for example, 31 designates an Al/Zr molar ratio of 3/1.

Primary Emulsion A	*% by Wt.*
PPG-11 stearyl ether	5.56
Polyoxyethylene(2)stearyl ether	4.07
Polyoxyethylene(20)stearyl ether	1.48
Perfume	0.74
Disodium edetate, dihydrate	0.25
FD&C Blue #1 (0.1% Aq. Sol.)	0.49
Water, deionized	87.41
	100.00

Ingredients	*% by Wt.*
Al/Zr trichlorohydrate 31 powder	10.00
ACH 50% solution	18.00
$AlCl_3 . 6H_2O$, 50% solution	6.00
Glycine	1.50
Water, deionized	24.00
Primary Emulsion A q.s. to	100.00

pH: 3.4 ± 0.3
Overnight viscosity: 500-1500 cps

EXAMPLE 14
Formula BA 1810-65

Aluminium zirconium trichlorohydrate 21 powder (Al/Zr molar ratio = 2/1) was used:

Ingredients	*% by Wt.*
Al/Zr trichlorohydrate 21 powder	10.00
ACH 50% solution	18.00
$AlCl_3 . 6H_2O$, 50% solution	6.00
Glycine	1.50
Water, deionized	24.00
Primary Emulsion A q.s. to	100.00

pH: 3.5 ± 0.3
Overnight viscosity: 500-1500 cps

EXAMPLE 15
Formula BA 1810-56

Aluminum zirconium octachlorohydrex - glycine powder 81 (Al/Zr molar ratio = 8/1) was used:

Ingredients	*% by Wt.*
Al/Zr octachlorohydrex - glycine powder 81	15.00
ACH 50% solution	10.00
$AlCl_3 . 6H_2O$ solution	8.00
Glycine	0.50
Water, deionized	26.00
Primary Emulsion A q.s. to	100.00

pH: 3.2 ± 0.3
Overnight viscosity: 500-1500 cps

EXAMPLE 16
Formula BA 1810-57

Aluminum zirconium pentachlorohydrate solution (Al/Zr molar ratio = 10/1) was used:

Ingredients	*% by Wt.*
Al/Zr pentachlorohydrate solution, 30%	35.00
ACH 50% solution	10.00
$AlCl_3 . 6H_2O$ 50% solution	8.00
Glycine	2.00
Water, deionized	4.50
Primary Emulsion A q.s. to	100.00

pH: 3.4 ± 0.3
Overnight viscosity: 450-1500 cps

EXAMPLE 17
Formula BQ 1856-83

Different buffering agent such as sodium carbonate is used as an additional buffering agent in this Example.

Primary Emulsion B	*% by Wt.*
PPG-11 stearyl ether	6.43
Polyoxyethylene(2)stearyl ether	4.71
Polyoxyethylene(20)stearyl ether	1.71
Perfume	0.86
Disodium edetate, dihydrate	0.29
FD&C Blue #1 (0.1% aq. sol.)	0.57
Water, deionized	85.43
	100.00

Ingredients	*% by Wt.*
Al/Zr tetrachlorohydrex - glycine solution, 35%	45.00
ACH, 50% solution	10.00
$AlCl_3 . 6H_2O$, 50% solution	8.00
Glycine	1.20
Sodium carbonate monohydrate	0.50
Water, deionized	0.30
Primary Emulsion B q.s. to	100.00

pH: 3.4 ± 0.3
Overnight viscosity: 500-1500 cps

EXAMPLE 18
Formula BQ 1856-83

Magnesium hydroxide was used as an additional buffering agent.

Ingredients	*% by Wt.*
Al/Zr tetrachlorohydrex - glycine solution, 35%	45.00
ACH, 50% solution	10.00
$AlCl_3 . 6H_2O$, 50% solution	8.00
Glycine	0.50
Magnesium hydroxide	0.50
Water, deionized	1.00
Primary Emulsion B q.s. to	100.00

pH: 3.4 ± 0.3
Overnight viscosity: 500-1500 cps

EXAMPLE 19
Formula 1509-61

Ingredients	*% by Wt.*
PPG-11 stearyl ether	2.25
Polyoxyethylene(2)stearyl ether	1.65
Polyoxyethylene(20)stearyl ether	0.60
Perfume	0.30
Water, deionized	41.20
Disodium edetate, dihydrate	0.10
DC Antifoam AF, 25%	0.10
Al/Zr tetrachlorohydrex - glycine solution, 35%	35.00
ACH, 50% solution	15.00
$AlCl_3 . 6H_2O$, 50% solution	3.00
Glycine	0.60
FD&C Blue #1 (0.1% aq. sol.)	0.20
	100.00

pH: 3.4 ± 0.3
overnight viscosity: 400-1200 cps

To demonstrate that the combination of aluminum chloride, ACH, aluminum zirconium polychlorohydrate and glycine act synergistically, a number of formulas identified in Table II below were prepared. Formula # 1908 is representative of the present invention.

TABLE II

Ingredients	% by Wt. based on Total Weight F #1052	F #1676	F #1908	F #1341	Commercial Emulsion Roll-On (BR-4504)
ACH (% anhydrous basis)	18.3	—	7.5	16.2	—
$AlCl_3 . 6H_2O$ (% anhydrous basis)	—	—	1.7	2.0	—
Al/Zr tetrachlorohydrate (% anhydrous basis)	—	18.6	9.3	—	Al/Zr trichlorohydrate (% anhy. basis) 19.7
Glycine	—	2.8	1.9	2.0	Glycine 4.2
PPG-11 stearyl ether	3.0	2.0	2.25	3.5	—
Polyoxyethylene(2) stearyl ether	1.9	1.5	1.65	2.3	PEG-40 stearate, Glyceryl stearate, Glycerin, Refined paraffin,
Polyoxyethylene(20) stearyl ether	1.1	0.6	0.6	1.2	Isopropyl palmitate, Mg/Al silicate and Fragrance
Disodium edetate, dihydrate	0	0.1	0.1	0.1	
Perfume & Color } Water q.s. to 100 }	→				
Total Actives	18.3	18.6	18.5	18.2	19.7 Total actives
Total Glycine	0	2.8	1.9	2.0	4.2 Total Glycine

As will be noted, each of these formulas is similar excepting for the active ingredients that are employed. Further, each contains the total active ingredients at essentially the same concentration i.e. about 18% on an anhydrous basis.

Each of these compositions was tested for antiperspirant activity. The general procedure employed was as described in Federal Register, Vol. 43, Number 196, October 10, 1978. It is called the gravimetric axillary antiperspirant test. Paired comparison (treated vs. treated) studies of the antiperspirant effectiveness of antiperspirant emulsion.

The details of the test procedure are given below.

Test Procedure

A random test pattern supplied by Statistical Services is employed, e.g. if one test material is evaluated, half of the panelists receives the test material under the left axilla while the remaining half receives it under the right. The opposite axilla serves as a control. If two test materials are evaluated, half the panel has product A applied to the left axilla and product B to the right while the remaining panelists have the reverse product/axilla allocations.

The test is conducted during a five-day period (Monday through Friday). Sweating is induced under environmental conditions of 100°F ± 2° and 40% relative humidity ± 2%.

Day 1: Control measurement followed by product application

Panelists wait one-half hour at room temperature (approximately 65°-80°F) after which time they enter the test room. They then place the untared Webril Pads (which are folded in half to a size of 4" × 2") in their axillae. Subjects sit in the test room for a 40 minute warm-up period. At the end of this period, the warm-up pads are removed by the panelists and are discarded.

The panelists remove the plastic bags containing the tared collection pads from the manila envelopes. The subjects insert the pads as directed by a technician. The pads remain in the axilla for a period of 20 minutes. After such time, the panelists are instructed to remove the pads and to place them into the designated plastic bags which are then returned to the manila envelopes.

The panelists exit the test room, hand in their envelopes, and then wash their axillae with tepid water with the aid of gauze pads and towel dry them. Approximately one to three minutes later, the test material is applied and the panelists leave. The plastic bags are removed from the manila envelopes and are weighed by a technician. Panelists must perspire at least 200 mg/axilla to continue participation on the panel.

Day 2: Product application only

Panelists wait one-half hour at room temperature, after which time they wash their axillae with tepid water with the aid of gauze pads and towel dry them. Approximately one to three minutes later, the test material is applied and the panelists leave.

Day 3: Product application and collection

Panelists wait one-half hour at room temperature, after which time they wash their axillae as described above. Approximately one to five minutes later the test material is applied. The panelists then wait one hour at room temperature. Then they enter the test room for a 40-minute warm-up and place the untared pads in their axillae. At the end of this period, the warm-up pads are removed and discarded.

The panelists remove the plastic bags containing the tared collection pads from the manila envelopes. They insert the pads as directed by a technician. The pads remain in the axillae for a period of 20 minutes. Then the panelists are instructed to remove the pads and to place them into the designated plastic bags which are then returned to the manila envelopes. The panelists exit the test room, hand in their

envelopes, and leave. The plastic bags are removed from the manila envelopes and are weighed by a technician.

Day 4: Product application only

Same as Day 2.

Day 5: Product application and collection

Same as Day 3.

The results of the test are summarized as follows:

I. Formula #1908 vs. Formula #1052

Results:

The data from this study, employing 47 female subjects, were submitted to the Statistical Services Department for evaluation.

Briefly, their analysis indicated that Antiperspirant Roll-on Formula #1908 was significantly more effective than Formula #1052 at the 0.01 level.

This conclusion is supported by the A/B ratio (amount of sweat collected from A treated axilla over B treated axilla) for the final treatment-collection day (adjusted by control) averaging 0.819 which is significantly different from 1.0 equality.

The above data indicates that Formula #1908 is about 18% more effective than Formula #1052.

II. Formula #1908 vs. Formula #1676

Results:

The data from this study, employing 46 female subjects, were submitted to the Statistical Services Department for evaluation.

Briefly, their analysis indicated that Formula #1908 was significantly more effective than Formula #1676 at the 0.01 level.

This conclusion is supported by the A/B ratio for the final treatment-collection day (adjusted for control) averaging 0.883 which is significantly different from 1.0 equality.

The above data indicates that Formula #1908 is about 12% more effective than Formula #1676.

III. Formula #1908 vs. Commercial Emulsion Roll-On Formula # BR 4504

Results:

The data from this study, employing 48 female subjects, were submitted to the Statistical Services Department for evaluation.

Briefly, their analysis indicates that Formula #1908 was significantly more effective than Commercial Emulsion Roll-On at the 0.01 level.

This conclusion is supported by the A/B ratio for the final treatment-collection day (adjusted for control) averaging 0.881 which is significantly different from 1.0 equality.

The above data indicates that Formula #1908 is about 12% more effective than Formula #BR 4504.

IV. Formula #1341 (see Table II) which contains as antiperspirant actives a combination of ACH and $AlCl_3 . 6H_2O$ (at a level of about 18.2) in a similar manner was shown to be on the average 9.6% less effective than the Commercial Emulsion Roll-on (BR 4504) which contains 19.7% Al/Zr trichlorohydrate as the antiperspirant active (see Table II). The latter, however, has also been shown to be less effective than Formula #1908 embodied in the present invention i.e. Formula #1908 was about 12% more effective than Formula #BR 4505 (see Paragraph III).

V. Formula #1991 (See Example 9) in a similar manner was shown to be 15% more effective than a commercial suspension roll-on product identified as Formula #BR 4751. The latter has the following composition:

Formula # BR 4751

Ingredients	*% by Wt.*
Aluminum zirconium tetrachlorohydrate (anhydrous basis)	13.8
Glycine	2.0
Bentone 38	3.25
Cyclomethicone and Perfume q.s. to	100.00

Although the invention has been described with reference to specific forms thereof, it will be understood that many changes and modifications may be made without departing from the ambit of this invention.

CLAIMS

1. An antiperspirant composition buffered to a pH in the range of from about 2.5 to about 4.5, said composition having incorporated therein as active ingredients aluminum chloride, aluminum chlorohydrate, and an aluminum zirconium polychlorohydrate complex, said aluminum zirconium polychlorohydrate complex having the formula:

(I) $Al_xZr(OH)_yCl_z.nH_2NCH_2COOH . nH_2O$

$-NH_2$.

wherein:

(a) x is a number from 2 to 10;
(b) Z is a number from 3 to 8;
(c) y equals $(3x + 4) - Z$;
(d) the sum of $y + Z$ is a number from 10 to 34;
(e) m is a number from 0 to 12;
(f) n is a number from 0 to 3

said active ingredients being incorporated in said composition in the following weight percentages based on the total weight of said composition and on an anhydrous basis:

(1) aluminum chloride from about 0.5% to about 6%
(2) aluminum chlorohydrate from about 1% to about 15%
(3) aluminum zirconium polychlorohydrate complex from about 5% to about 16%.

2. A composition according to Claim 1 including an additionally added buffering agent.

3. A composition according to Claim 2 in which the additionally added buffering agent is glycine.

4. A composition according to Claim 3 in which the total amount of glycine in bound and/or unbound form is present in said composition at a level in the range of from about 0.5% to about 5% by weight based on the total weight of the composition.

5. A composition according to any preceding Claim wherein the aluminum chloride is incorporated as the aluminum chloride hexahydrate.

6. A composition according to any preceding Claim in which the aluminum zirconium polychlorohydrate complex is aluminum zirconium tetrachlorohydrate glycine.

7. A composition according to any of Claims 1 to

wherein the aluminum zirconium polychlorohydrate complex is selected from the group consisting of aluminum zirconium tetrachlorohydrate; aluminum zirconium tetrachlorohydrate glycine; aluminum zirconium trichlorohydrate; aluminum zirconium trichlorohydrate glycine; aluminum zirconium pentachlorohydrate; aluminum zirconium pentachlorohydrate glycine; aluminum zirconium octachlorohydrate; aluminum zirconium octachlorohydrate glycine and mixtures thereof.

8. A composition according to Claim 7 wherein the aluminum chloride is incorporated as the hexahydrate.

9. An antiperspirant composition buffered to a pH in the range of from about 2.8 to 3.8, said composition having incorporated therein as active ingredients aluminum chloride, aluminum chlorohydrate, an aluminum zirconium polychlorohydrate complex and containing glycine, said aluminum zirconium polychlorohydrate complex having the formula:

(I) $Al_xZr(OH)_yCl_z.nH_2NCH_2COOH \cdot mH_2O$
$-NH_2$

wherein:

(a) x is a number from 2 to 10;
(b) Z is a number from 3 to 8;
(c) y equals $(3x + 4) - Z$;
(d) the sum of $y + Z$ is a number from 10 to 34;
(e) m is a number from 0 to 12;
(f) n is a number from 0 to 3

said active ingredients being incorporated in said composition in the following weight percentages based on the total weight of said composition and on an anhydrous basis:

(1) aluminum chloride from about 1.5% to about 3.3%
(2) aluminum chlorohydrate from about 2% to about 10
(3) aluminum zirconium polychlorohydrate complex from about 8% to about 14%

the total weight percent of glycine in bound and/or unbound form being from about 1.5% to about 3% based on the total weight of the composition.

10. A composition according to Claim 9 wherein the aluminum chloride is incorporated as the aluminum chloride hexahydrate.

11. A composition according to Claim 9 or 10 in which the aluminum zirconium polychlorohydrate complex is aluminum zirconium tetrachlorohydrate glycine.

12. A composition according to Claim 9 or 10 wherein the aluminum zirconium polychlorohydrate complex is selected from the group consisting of aluminum zirconium tetrachlorohydrate; aluminum zirconium tetrachlorohydrate glycine; aluminum zirconium trichlorohydrate; aluminum zirconium trichlorohydrate glycine; aluminum zirconium pentachlorohydrate; aluminum zirconium pentachlorohydrate glycine; aluminum zirconium octachlorohydrate; aluminum zirconium octachlorohydrate glycine and mixtures thereof.

13. A composition according to Claim 12 wherein the aluminum chloride is incorporated as the hexahydrate.

14. A composition according to Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13 in the form of a oil-in-water emulsion in which at least a large component of the active ingredients and the glycine are contained in the water phase.

15. A method for inhibiting perspiration in a subject which comprises applying to the skin of said subject an effective amount of the composition of Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 or 13.

16. A composition as claimed in claim 1 or 9, substantially as described in any of the foregoing Examples.

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(71) Applicants Bristol-Myers Company, 345 Park Avenue, New York 10154, United States of America.
(72) Inventors Leonard Weintraub, Allan H. Rosenberg.
(74) Agents Carpmaels and Ransford, 43, Bloomsbury Square, London WC1A 2RA.

(54) **An antiperspirant combination containing an aluminum halohydrate and a stannic halide.**

(57) An antiperspirant combination contains an aluminum halohydrate and a stannic halide and also preferably contains a neutral amino acid. The combination corresponds to the empirical composition $[Al_2(OH)_aX.nH_2O]_b$ $[SnY_4.n^1H_2O]_c$ [Neutral Amino Acid]$_c$, wherein
(a) X and Y are holgen;
(b) n and n^1 are 0 to 6;
(c) the ratio of weight of a/b is 0.3 to 1.8; and
(d) the ratio by weight of c/b is 0 to 1.3. Material is in powder form or incorporated in liquid or solid vehicle.

GB 2 097 675 A

SPECIFICATION

An antiperspirant combination containing an aluminum halohydrate and a stannic halide

This invention relates to new antiperspirant combinations which are highly effective and have a low irritation potential for skin. More particularly, it concerns antiperspirant combinations containing a stannic halide, an aluminium halohydrate as active antiperspirant ingredients and which may also contain a neutral amino acid.

There have been some suggestions in the prior art for using tin salts such as tin chloride in a shaving cream preparation which will tend to stop or deodorize perspiration. Such compositions are described in U.S. Patent 2,145,583. Similarly, there has been some vague teaching for using metallic salts of mineral acids e.g. tin salts of hydrochloric acid to inhibit perspiration (see U.S. Patent 2,236,387). To reduce the corrosive action of these materials, the patentee recommends the use of, among other things, amino acids e.g. glycine. Compositions of this character, however, left much to be desired both from the point of view of irritation potential and/or activity.

It has now been found that highly effective antiperspirant combinations of low irritation potential for skin can be provided by mixing a stannic halide with an aluminum halohydrate preferably together with a neutral amino acid.

One of the mechanisms believed to contribute to the antiperspirant effectiveness of metal salts is their ability to form obstructive hydroxide gels in the sweat ducts. Metal salts are believed to hydrolyze to form acidic solutions that diffuse into the sweat ducts and then form insoluble hydroxide on being neutralized by the sweat present in the ducts. Their ability to form hydroxide plugs (as a function of the sweat pH), the type of plug formed (i.e. gelatinous or crystalline) and the depth of penetration into the sweat duct all appear to contribute to the antiperspirant activity of metal salts.

It has been found by *in vitro* diffusion studies that antiperspirant combinations of the present invention in solution have the properties that are consistent with effective antiperspirant activity. These solutions diffuse quite deeply into capillary tubes before precipitation occurs. Furthermore, gelatinous precipitates are formed at relatively low pH (5.0).

Moreover, animal toxicity data indicate that the combinations embodied in this invention are non-toxic and non-irritating. This has been demonstrated in animal studies at concentrations in the range of from 16 to 48%.

It is accordingly an object of the present invention to provide an effective antiperspirant combination containing an aluminum halohydrate and a stannic halide that may also contain a neutral amino acid and that is low in irritation potential for skin.

Other and more detailed objects of this invention will be apparent from the following description and claims.

The antiperspirant combinations of the present invention correspond to the empirical composition:

(I) $[Al_2(OH)_5X \cdot nH_2O]_a \cdot [SnY_4 \cdot n'H_2O]_b \cdot [\text{Neutral Amino Acid}]_c$

wherein:

(1) X and Y are halogen, preferably chlorine;
(2) n and n' are numbers from 0 to 6;
(3) the ratio by weight of a/b is from about 0.3 to about 1.8; and
(4) the ratio by weight of c/b is from 0 to about 1.3.

This corresponds to a mole ratio of Al/Sn of from about 1 to about 6 and a mole ratio of neutral amino acid/Sn of from 0 to about 6. The preferred neutral amino acid is glycine.

The incorporation of a neutral amino acid and particularly glycine in the present antiperspirant combinations, although it is an optical feature, is highly desirable. Aluminium chlorohydrate, for example, when added to $SnCl_4 \cdot 5H_2O$ solution reduces the acidity of the solution and within certain ranges of concentration provide solutions that are stable with respect to gellation. This range of stability can be increased by the addition of a neutral amino acid such as glycine.

Two antiperspirant combinations falling within the above definition have been found to be particularly suitable. One combination identified hereinafter as SnAG A corresponds to Formula I above in which glycine is the amino acid, chloride is the halogen, n=2, n'=5, and is characterized by the following weight ratios:

a/b = 1.11 c/b = .22

A second combination identified hereinafter as SnAg B corresponds to Formula I above in which glycine is the amino acid, chloride is the halogen, n=2, n'=5, and is characterized by the following weight ratios:

a/b = 1.11 c/b = .43

The antiperspirant combinations of the present invention are prepared by mixing the aluminum halohydrate, the stannic halide and, when employed, the amino acid in solution. It is not clear whether a true molecular complex is formed in the process or whether a simple mixture is formed. Consequently, as used herein, the term antiperspirant combination is intended to include true molecular complexes of the various ingredients or mere mixtures thereof.

The antiperspirant combinations of the present invention are generally prepared by forming a solution, usually an aqueous solution, of the ingredients in the appropriate ratios. The solution is then dried to remove the solvent and form a dry powder. Various processes are known in the art to obtain the requisite dried product. These include evaporation under vacuum, spray drying etc. The dried powder can then be used to formulate various products.

However, the solution of the antiperspirant combination described above can be used as such as an antiperspirant agent without first drying the solution to form a powder. Furthermore, when the final product is to take the form of a solution containing the solvent used to prepare the combination or to form an emulsion in which the solution of the antiperspirant combination forms all or part of a phase of said emulsion, the solution of the antiperspirant combination may also be used directly i.e. without first going through a drying step.

The antiperspirant combinations of the present invention may be used in a variety of dosage forms. Thus, they may be used in the form of simple solutions in solvents in which they are sufficiently soluble e.g. water, alcohol, hydro-alcoholic solvents. These may be dispensed by means of the conventional roll-on applicators widely used in this art or other types of applicators suitable for dispensing solutions of this character. These solutions may also be dispensed in the form of pads which have been saturated with these solutions.

The antiperspirant combination of the present invention may be used in the form of a suspension type product. In this case, the dried product could be distributed in a vehicle in which it is suspendable but not soluble. These will usually be hydrophobic vehicles which can be exemplified by such materials as silicones such as cyclomethicone and dimethicone, esters such as isopropyl myristate or dibutyl phthalate, long chain fatty alcohols such as stearyl alcohol and glycols such as propylene glycols, etc. These too could be dispensed in the form of a roll-on applicator.

In a similar fashion, the antiperspirant combinations of this invention, in form of a solution, could be formulated into emulsion type products to be dispensed from roll-on type applicators or aerosol dispensers or may be incorporated in creams, ointments. In the dry form, these materials can be included as the active ingredients in antiperspirant stick products or dispensed as a powder.

The quantity of the present antiperspirant combination, which may or may not contain the amino acid, that will be contained in products in accordance with the present invention will vary depending on the particular dosage form and the degree of activity required. Usually, however, on a dry basis it will comprise from about 3% to about 50% by weight based on the total weight of the composition and preferably, from about 15% to about 30% on the same weight basis.

The following Examples are given to further illustrate the present invention. It is understood, however, that the invention is not limited thereto.

EXAMPLE 1

Preparation of SnAG A Powder

In a glass beaker, 185 g. of glycine is added to 1910 g. of a 50% aqueous solution of aluminum chlorhydrate. The mixture is stirred by means of a magnetic stirrer until a clear solution is obtained. (This solution is called Solution I).

In another glass beaker, 860 g. of stannic chloride pentahydrate is added to 1209 g. of deionized water. The mixture is heated to approximately 50°C (by means of hot plate) and stirred until a clear solution is obtained. (This solution is called Solution II).

Solution I is slowly added to Solution II with stirring until a uniform, clear solution is obtained. SnAG A solid is obtained from the resultant aqueous SnaG A solution by evaporating the solution under vacuum (using a one stage vacuum pump at less than 10 torr) at 70°C by means of a Buchi Roto-Vapor. The resultant SnAG A solid is ground in a mortar and pestle and then redried for one hour at 70°C in the Roto-Vapor. The redried solid is then re-ground in a mortar and pestle and stored.

In an alternative procedure, the drying operation can be accomplished by spray drying the clear solution obtained from mixing Solution I and Solution II above. In this procedure, a Niro Atomizer is employed in which the inlet temperature is maintained at 200°C and the outlet temperature is maintained in the range of about 122°C to 130°C.

A 20% aqueous solution of the solid obtained from the above processes has a pH of 3.3; whereas, a 16% solution had a pH of 3.5.

EXAMPLE 2
Preparation of SnAG B Powder
Using the same procedure outlined above, SnAG B powder was produced. However, in this instance, the following quantities of starting materials are employed:

Glycine	233 g.
Aluminum Chlorhydrate (50% solution)	1200 g.
Stannic Chloride Pentahydrate	540 g.
Deionized water	900 g.

A 20% aqueous solution of the solid obtained by this process had a pH of 3.5; whereas, a 16% solution had a pH of 3.7.
The following Examples 3, 3A, 4 and 5 are aqueous compositions of SnAG A and SnAG B that are useful as antiperspirants:

EXAMPLE 3
Formula 1976

Ingredients	*% by Wt.*
SnAG A (powder)	24.00
Deionized water	76.00

Appearance: Clear solution
Color: Water white to slightly yellow
pH: 3.1 ± 0.5
Total SnAG A in Formula: 24.0 ± 2.4%

EXAMPLE 3A
A composition like Formula 1976 is prepared, excepting that 12% SnAG A powder is used with 88% deionized water.

EXAMPLE 4
Formula 1977

Ingredients	*% by Wt.*
SnAG B (powder)	24.00
Deionized water	76.00

Appearance: Clear solution
Colour: Water white to slightly yellow
pH: 3.3 ± 0.5
Total SnAG B in Formula: 24.0 ± 2.4%

EXAMPLE 5
Formula 1978

Ingredients	*% by Wt.*
SnAG A (powder)	48.00
Deionized water	52.00

Appearance: Clear to slightly hazy solution
Color: Water white to slightly yellow
pH: 2.3 ± 0.5
Total SnAG A in Formula 48.0 ± 4.8%

The following Examples are given in tabular form (Table I). These illustrate a variety of aqueous compositions containing varying amounts of the ingredients contained in the antiperspirant combination of the present invention. The various mole ratios of materials are specified in the Table.

TABLE I
SnAG Compositions

Compound	Component Wgt. (g) ACH (50%)	$SnCl_4.5H_2O$	Glycine	H_2O	Weight % Solids	pH	Mole Al/Sn	Ratios Al/Glycine	Glycine/Sn
SnAG III	100	30.5	13.3	100	38	3.1	5.5	2.7	2.0
SnAG I	200	61	26.7	100	48	2.7	5.5	2.7	2.0
SnAG VIII	100	30.5	6.6	44.4	48	2.4	5.5	5.5	1.0
SnAG V	100	45	19.4	75	48	2.7	3.7	1.8	2.0
SnAG VI	100	45	9.7	63.3	48	2.4	3.7	3.7	1.0
SnAG IV[a]	100	15.3	13.3	100	34	3.5	10.9	2.7	4.0
a = SnAG IV Solution Slightly Hazy									
SnAG A	1910	859.5	185.3	1209	48	2.4	3.7	3.7	1.0
SnAG B	1200	540	232.8	900	48	2.7	3.7	1.8	2.0

Solid SnAG I, VI, A and B are obtained by evaporating from solution.
Solids are off-white, granular and quite hygroscopic.

pHs of 20% and 16% solutions of solid A and B are 3.3, 3.5 and 3.5, 3.7 respectively.

EXAMPLE 6
SnAG Suspension Roll-On 1944-3

Ingredients	*% (w/w)*
Bentone 38	2.50
Anhydrous Alcohol, SD-40	2.00
SnAG A powder	24.00
Cyclomethicone 7158	71.30
Perfume	0.20
	100.00

EXAMPLE 7
SnAG Roll-On 1944-4

Ingredients	*% (w/w)*
Polyoxypropylene fatty alcohol ethers, E-SP	4.00
Polyoxyethylene (2) stearyl ether	2.90
Polyoxyethylene (20) stearyl ether	1.10
Butylated hydroxytoluene	0.05
Disodium edetate, dihydrate	0.10
Deionized water	67.35
SnAG B powder	24.00
Perfume	0.30
Color	0.20
	100.00

EXAMPLE 8
SnAG Solid Stick 1944-5

Ingredients	*% (w/w)*
Stearyl alcohol	10.00
Hydrogenated caster oil MP-80	3.00
Paraffin Wax FT 300	3.00
Butylated hydroxytoluene	0.05
Cyclomethicone 7158	52.75
Talc 5251	7.00
SnAG A powder	24.00
Perfume	0.20
	100.00

Precipitation Studies

SnAG solutions at concentrations of 3.8% and 16% were diffused into glass capillaries containing a buffer solution at pH 5.0 at room temperature. The capillaries were 2.5 inches long with a 0.5 mm I.D. The buffer pH was chosen to represent the low pH range of human sweat. The capillaries were filled with buffer solution and then placed in beakers containing SnAG solutions. Time to form precipitate, distance of precipitate from capillary tip and any other visual changes were recorded. Distance of precipitate from capillary tip was measured with a cathetometer. A high intensity lamp was used for illumination.

The results of these tests are summarized in Table II below:

TABLE II

Solution	Time to Form Precipitate (min.)	Distance of Precipitate from Capillary Tip (mm.)
16% SnAG I	1	8.8
3.8% SnAG I	Immediate	7.5
16% SnAG VI	1	10.7
3.8% SnAG VI	Immediate	7.8

In contrast to the results obtained in these tests, aluminium chlorohydrate (ACH) solutions did not precipitate at pH 5 and below. Zirconium aluminium chlorohydrate glycine (ZAG) solutions precipitated at pH 5 but did not diffuse beyond the capillary tip.

Although the invention has been described with reference to specific forms thereof, it will be understood that many changes and modifications may be made without departing from the ambit of this invention.

CLAIMS

1. An antiperspirant combination corresponding to the empirical composition:

$$[Al_2(OH)_6X \cdot nH_2O]_a \cdot [SnY_4 \cdot n'H_2O]_b \cdot [\text{Neutral Amino Acid}]_c$$

wherein:
(a) X and Y are halogen;
(b) n and n' are numbers from 0 to 6;
(c) the ratio by weight of a/b is from about 0.3 to about 1.8; and
(d) the ratio by weight of c/b is from 0 to about 1.3.

2. An antiperspirant combination according to Claim 1 corresponding to the empirical composition:

$$[Al_2(OH)_5Cl \cdot 2H_2O]_a \cdot [SnCl_4 \cdot 5H_2O]_b \cdot [\text{glycine}]_c$$

3. An antiperspirant combination according to Claim 1 or 2 in the form of a dry powder.
4. An antiperspirant combination according to Claim 1 or 2 contained in a liquid vehicle.
5. An antiperspirant combination according to Claim 4 wherein said liquid vehicle is an aqueous vehicle.
6. An antiperspirant combination according to Claim 1 or 2 contained in an antiperspirant stick vehicle.
7. An antiperspirant combination according to any preceding Claim 2 in which the weight ratio of a/b is about 1.11 and the weight of c/b is about .22.
8. An antiperspirant combination according to any preceding claim in which the weight ratio of a/b is about 1.11 and the weight ratio of c/b is about .43.
9. An antiperspirant composition comprising a vehicle having incorporated therein from about 3% to about 50% by weight based on the total weight of said composition of the antiperspirant combination defined in Claims 1, 2, 3, 7 or 8.
10. A composition according to Claim 9 wherein said vehicle is a liquid vehicle.
11. A composition according to Claim 10 wherein said liquid vehicle is an aqueous vehicle.
12. An antiperspirant composition comprising a vehicle having incorporated therein from about 15% to about 30% by weight based on the total weight of said composition of the antiperspirant combination defined in Claims 1, 2, 3, 7 or 8.
13. A composition according to Claim 12 wherein said vehicle is a liquid vehicle.
14. A composition according to Claim 13 wherein said liquid vehicle is an aqueous vehicle.
15. A composition according to Claim 9 or 12 wherein said vehicle is an antiperspirant stick vehicle.
16. A process for inhibiting perspiration in a subject which comprises applying to the skin of such subject

an effective antiperspirant quantity of the compositions defined in Claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15.

17. An antiperspirant combination according to claim 1, substantially as described in Example 1 or 2 herein.

18. A composition according to claim 9 or 12, substantially as described in Example 3, 3A, 4, 5, 6, 7 or 8, or Table I, herein.

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(71) Applicant Colgate-Palmolive Company, (USA—Delaware), 300 Park Avenue, New York, New York 10022, United States of America
(72) Inventor Frank William Marschner
(74) Agent and/or address for service Kilburn and Strode, 30, John Street, London, WC1N 2DD

(54) **Deodorant composition**

(57) A deodorant composition contains zinc glycinate in a cosmetically acceptable vehicle. Cream, aerosol and roll-on compositions are exemplified.

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SPECIFICATION
Deodorant compound

The present invention relates to zinc glycinate as a deodorant active material having the dual function of chemically neutralizing body odours and inhibiting bacterial growth, particularly gram negative bacteria.

The prior art is replete with antiperspirant compositions containing zinc salts per se or in combination with aluminium and/or zirconium salts, as the active antiperspirant agent. The Journal of the American Pharmaceutical Association, Vol. XLVII, No. 1, Jan. 1958, pages 25—31 discloses combinations of zinc methionate and aluminium sulphamate, and zinc sulphate in combination with aluminium methionate. The Chemistry and Manufacture of Cosmetics by Maison G. de Navarre, 1941, page 261 lists the zinc salts in common use as antiperspirants to include the sulphate, chloride and sulphocarbonate; and further lists other zinc salts worth investigating which include benzoate, citrate, formate, glycerophosphate, perborate, salicylate, zinc-ammonium sulphate and zinc-potassium sulphate. U.S. Patent No. 2,586,289 discloses zinc sulphamate as the antiperspirant in a cream base (oil-water emulsion); and U.S. Patent No. 2,890,987 discloses zinc chloride in a stick form astringent. U.S. Patent No. 3,325,367 discloses zinc sulphamate and zinc phenol sulphonate as antimicrobial astringent metal salts useful in antiperspirant creams, lotions, sticks and powders. U.S. Patent No. 3,856,941 discloses astringent gels containing a mixture of aluminium salts with other metallic salts such as zinc salts including zinc chloride, zinc sulphate and zinc nitrate. U.S. Patents No. 4,045,548 and No. 4,018,887 disclose dry powder antiperspirant agents including zinc sulphate, zinc sulphocarbonate and a zinc-aluminium complex in an aerosol antiperspirant composition. All of the aforesaid zinc compounds function as antiperspirants which restrict the flow of perspiration as a means of combating unpleasant body odours.

The suppression of secretion of perspiration is known to have unfavourable effects on the skin, particularly skin irritation; and may also be corrosive to fabrics in contact therewith. This has led to the use of anticorrosive agents in conjunction with antiperspirants as shown in U.S. Patent No. 2,350,047, wherein a water insoluble metallic anticorrosive agent such as a zinc, magnesium or aluminium oxide, hydroxide or carbonate is added to an antiperspirant composition containing a water soluble astringent salt such as aluminium chloride or sulphate.

The prior art also discloses glycinates such as aluminium zirconium glycinate chelates as antiperspirant agents which restrict the flow of perspiration as noted in U.S. Patents No. 4,049,792, No. 3,792,068 and No. 4,083,956 and British Patent No. 1,572,116. An amino acid, such as glycine, has been added to an antiperspirant composition as an inhibitor of discolouration caused by the aluminium sulphamate antiperspirant, as shown in U.S. Patent No. 2,586,288; and as a protective colloid to inhibit the corrosive action of astringent salts such as aluminium or zinc chloride or sulphate, as shown in U.S. Patent No. 2,236,387.

Another method of combating body odours is the formulation of a deodorant composition containing a deodorant active agent which does not inhibit the flow of perspiration to any appreciable extent. U.S. Patent No. 3,172,817 discloses a water soluble beta diketone zinc salt as an effective deodorant in sanitary napkins, diapers, insoles, creams, soaps, liquids, and body powders. U.S. Patent No. 3,996,346 discloses a deodorant and antiperspirant composition containing zinc oxide and phenol which react in situ to form zinc phenate.

U.S. Patent No. 4,172,123 discloses a deodorant composition containing a zinc salt of an unsaturated hydroxy-carboxylic acid having 17 to 21 carbon atoms, such as zinc ricinoleate as the odour binding agent. The zinc ricinoleate is described as having odour-binding and fungistatic activity.

European Application No. 0-024-176 by Unilever discloses deodorant compositions comprising a suspension of zinc carbonate as the deodorant active material, which reduces axillary body odour without suppressing the secretion of perspiration.

U.K. Patent Application G.B. 2,052,978 A discloses a zinc-glycine combination in solution at a pH of 4.5—8.0 as an anticalculus-antiplaque agent in an oral composition. The zinc salt may be added to the mouthwash as zinc glycinate directly or the zinc salt and the glycine may be added separately. The zinc ions are kept in solution at pH 4.5—8 by using glycine.

However, there is no disclosure of zinc glycinate as a deodorant active material possessing the dual function of inhibiting bacterial growth and chemically neutralizing body odours.

The primary object of the invention is to provide a novel non-irritating, highly effective deodorant compound which neutralizes unpleasant odours through chemical interaction and also inhibits bacterial growth.

The invention also aims to provide deodorant compositions which are substantially non-irritating to the body, containing a zinc glycinate compound as the essential antibacterial active agent.

The invention further aims to provide a deodorant composition containing anhydrous or hydrated zinc glycinate as the essential deodorant agent.

The invention also aims to provide deodorant compositions containing zinc glycinate, which may be in the form of a liquid, cream, gel, solid sticks, powder or spray.

The invention also aims to provide a process for deodorizing odourous body locations by

contacting with a deodorizing amount of a compound which is a zinc glycinate in anhydrous or hydrated form.

According to the present invention a deodorant product comprises a deodorizing amount of zinc glycinate in a non-toxic cosmetically or dermatologically acceptable vehicle. The vehicle may be a powder such as talcum powder or foot powder; a lotion such as a roll-on composition; a cream base (oil-water emulsion); a gel such as a deodorant stick; or an aerosol or non-aerosol spray.

More specifically, the present invention relates to zinc glycinate as a novel deodorant agent which chemically neutralizes body odours and inhibits bacterial growth, suspended or dissolved in a cosmetically acceptable vehicle; and to a process of deodorizing the human body by contacting said odoriferous locations with said zinc glycinate-containing deodorant compositions.

Zinc glycinate was reported as synthesized by J. V. Dubsky and A. Rabas in Chem. Abstracts Vol. 24, 4722 (1931), by boiling glycine with a zinc oxide solution. The reaction product is described as a zinc metal amino acid complex which exists as the bis (glycino) - zinc (II) monohydrate $(NH_2CH_2COO)_2$—$Zn \cdot H_2O$.

It has been found that anhydrous zinc glycinate can be obtained by precipitating zinc glycinate from an alcoholic solution and using an excess amount of the glycine reactant to lower the solution pH and permit all the zinc oxide to react. More specifically, glycine and zinc oxide are added to water and the mixture is heated to 93°C and mixed until a clear solution is obtained. Absolute ethanol is then admixed therewith, which precipitates out zinc glycinate, leaving residual glycine in solution. The soft, white, nonhygroscopic crystals are filtered, washed with absolute ethanol, and dried in a vacuum oven or air dried. Analyses of the compound showed it to contain zinc and glycine ratios typical of anhydrous zinc glycinate. Its infrared spectrum resembled that of nickel glycinate. The reaction proceeds according to the following equation:

1. $$ZnO+2(NH_2CH_2COOH)\rightarrow(NH_2CH_2COO)_2Zn+H_2O$$

Analysis	*%*	*Analyzed ratio*	*Theoretical ratio*
Zinc	31.7	32.45	30.62
Glycine	66.0	67.55	69.38
Water	2.5		

The zinc glycinate is an odourless, low density, white, non-hygroscopic crystalline material, insoluble in ethanol and slightly soluble in water, having a solubility of about 6 grams per 100 ml cold water. The pH of a 1% aqueous solution of zinc glycinate is about 8.0 (within the range of 7.9 to 8.7).

It has also been found that zinc glycinate can be prepared by reacting a zinc halide, such as the chloride, with glycine according to the following equation:

2. $$ZnCl_2+2(HOOC—CH_2NH_2)+2\ NaOH\rightarrow Zn(OOC—CH_2NH_2)_2+2NaCl+2H_2O$$

In this method, zinc chloride and glycine are also reacted at elevated temperatures in an aqueous medium until a clear solution is obtained, but the zinc glycinate is precipitated by the addition of sodium hydroxide.

Still another method of producing zinc glycinate has been found, which utilizes the reactants zinc carbonate and glycine, as illustrated by the following equation:

3. $$ZnCo_3+2(HOOC—CH_2NH_2)\rightarrow Zn(OOC—CH_2NH_2)_2+CO_2+H_2O$$

In this method, the zinc carbonate is added to an aqueous solution of glycine. The CO_2 is liberated and the solution is evaporated to dryness or spray dried to obtain white crystals of zinc glycinate. This method does not require the addition of a precipitating agent such as ethanol or sodium hydroxide as in the first two methods explained above, rendering it a more commercially viable method (less costly and more direct).

It has been found that zinc glycinate and deodorant products containing zinc glycinate are highly effective, both for odour prevention as well as for neutralizing existing body odours such as underarm odours, foot odours and the like. In vitro deodorant tests showed that a solution of synthetic sweat odour was completely deodorized by zinc glycinate. In vivo deodorant tests using a 1% aqueous solution of zinc glycinate swabs on armpits with moderate to heavy odour resulted in complete deodorization of the armpits. Deodorant compositions containing zinc glycinate, such as unperfumed roll-on products containing 10% zinc glycinate in suspension, also showed instantaneous deodorizing of existing odours as well as the prevention of odour formation for periods as long as 48 hours.

The deodorant mechanism of zinc glycinate is similar to that of sodium bicarbonate, namely the neutralization of odours through acid/base chemical interaction. However, sodium bicarbonate hydrolyzes to form sodium hydroxide (NaOH), whereas zinc glycinate forms $Zn(OH)_2$, which is a milder base with lower potential skin sensitivity. The deodorant capacity of zinc glycinate (the weight required

to chemically neutralize the odour of x ml of synthetic sweat solution) is about the same as sodium bicarbonate. Zinc glycinate solutions, however, are pH stable, whereas sodium bicarbonate solutions are not, since they release CO_2 and gradually form sodium carbonate, a known skin irritant.

It has additionally been found that zinc glycinate also provides superior antibacterial properties compared to sodium bicarbonate. Using the Halo test and measuring the Zone of Inhibition in mm, using 150×25 mm plastic plates and 12.7 mm disks, the following comparative results were obtained.

Table 2

	Zone of inhibition	
Organism	*5% Aqueous sodium bicarbonate*	*5% Aqueous zinc glycinate*
Staph. aureus	0	partial inhibition
E. Coli	0	19.5 mm
P. Aeruginosa 10145	0	partial inhibition

Zinc glycinate is effective in aqueous solutions, in suspensions of various types and in powder form. Although zinc glycinate is not an antiperspirant, it can be incorporated into practically all antiperspirant type formulations by those familiar with the art. Various deodorant forms include aqueous solutions, alcoholic or cyclomethicone suspensions, pastes, creams, aerosol or non-aerosol sprays and solid sticks which incorporate volatile or non-volatile polar or non-polar vehicles.

Polar non-volatile vehicles may include polyhydric alcohols such as glycerine, propylene glycol, butylene glycol or polyglycols or ethoxylated glycols thereof, or polyethylene glycol.

Non-polar non-volatile vehicles may include emollient oils such as isopropyl myristate, isopropyl palmitate, octyl palmitate, fatty alcohols, fatty amides, ethoxylated or propoxylated fatty alcohols or acids, fatty glycerides or silicone.

Polar volatile vehicles may include water and monohydric alcohols such as ethanol, isopropanol or methanol.

Non-polar volatile vehicles may include hydrocarbons, fluorinated hydrocarbons, and cyclomethicones or mixtures thereof.

Other suitable bases for zinc glycinate are talc, starch, modified starches, oat powder, or other mineral or grain derived powders with particle sizes ranging between 5 and 100 microns which impart a smooth non-gritty feel on the skin.

Deodorant compositions in accordance with this invention will usually comprise about 1 to 20% zinc glycinate in solution or suspension form and may contain upwards of 50% in powder type products.

Certain ingredients to be avoided in zinc glycinate formulations which deactivate its deodorant properties include inorganic or organic acids. Also water soluble metal salts of fatty acids such as sodium stearate will generally react with zinc glycinate in the presence of water to form insoluble zinc stearate.

More specifically, the non-toxic cosmetically or dermatologically acceptable vehicle may be in the form of a lotion which comprises a liquid carrier such as a volatile lower alcohol or an aqueous alcoholic media, preferably ethanol containing a lesser amount of water, having particular utility in a roll-on composition. Usually the liquid carrier also comprises a suspending or thickening agent such as fumed silica, hydroxyethyl cellulose and other cellulose derivatives, hydrophobic clays, and combinations thereof, to maintain the zinc glycinate deodorant powder in suspension. Non-volatile polar or non-polar ingredients may be added to effect the deposition of a dry, non-sticky invisible film on the skin upon evaporation. The said non-volatile agents include polyhydric alcohols such as glycerine, propylene glycol and butylene glycol and polyglycols thereof, and emollient oils such as wheat germ oil, and any other alcohol soluble oils including isopropyl myristate, isopropyl palmitate, other fatty esters, fatty amides, fatty alcohols, fatty ethers such as stearyl ether, ethoxylated fatty alcohols or acids. The amount of emollient present is minor, about 1—5%. Roll-on compositions (dispensed from a roll-on container) in accordance with this invention will usually comprise about 10—20% deodorant active powder, about 0.1—2% suspending agent, about 10—30% non-volatile polar ingredients such as polyhydric alcohols, in a liquid carrier containing about 55—75% monohydric alcohol and 5—25% water.

The vehicle may also be in the form of a cream which usually comprises an emulsion of a fatty material in water. Fatty materials may include fatty esters, cetyl alcohol, ethoxylated fatty alcohols, fatty glycerides, and emollients as listed above. The water content of the cream may constitute about 25—70% of the cream base and with a deodorant active agent content of about 5—15%.

The cream may also be an anhydrous cream comprising a volatile silicone vehicle such as cyclomethicone containing emollients, suspending agents, thickening agents and other suitable ingredients to produce a product of desired consistency.

The zinc glycinate deodorant powder of this invention may also be suspended in a stick base vehicle which usually comprises a monohydric or polyhydric alcohol or combination thereof gelled with a fatty alcohol or fatty amide. This base may also contain emollients, suspending agents and other non-volatile polar and non-polar ingredients as set forth in the aforedefined roll-on formulations.

The zinc glycinate deodorant powder may also be suspended in a liquid vehicle comprising a carrier liquid and a liquified gaseous propellant to formulate an aerosol spray. Additional conventional ingredients as described above may be added, to effect a suitable deodorant spray product.

The vehicle may also be an oil base as in an ointment formulation, wherein the zinc glycinate is intimately admixed with the oil and fatty acid esters.

Another suitable base for the zinc glycinate deodorant is talc as in a talcum powder product.

The amount of the powdered zinc glycinate deodorant present in the deodorant compositions may vary over a wide range and may be as high as 50% by weight, as in ointments or talcum powders. However, about 1—20% is the preferred range in most cosmetic compositions.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

All amounts of various ingredients are by weight unless otherwise specified.

Preparation of zinc glycinate

Example 1

Components	*Amount*
$ZnCl_2$	13.6 gm
Distilled water	62.9 gm
Glycine	7.5 gm
NaOH (50% soln.)	16.0 gm

13.6 gms of $ZnCl_2$ (1 mole) were dissolved in 62.9 gms of hot distilled water and 7.5 gms of glycine (1 mole) was added to the $ZnCl_2$ solution. A clear solution was obtained. NaOH was added, resulting in the formation of a precipitate which was filtered out of solution, washed with ethanol, and air dried overnight. The precipitate crystals have a pH of 8.0, that of zinc glycinate.

The zinc glycinate crystals were added to a synthetic sweat solution containing the odourous fatty acid components of human sweat, such as acetic acid, and isovaleric acid. The addition of the zinc glycinate caused the pH of the fatty acid solution to rise to 7.0 and the solution was completely deodorized. Zinc glycinate deodorizes within the pH range 8 and 7.

Example 2

Components	*Amount (gms)*
$ZnCl_2$	13.6 (1 mole)
Glycine	15.0 (2 moles)
50.5% NaOH soln.	15.8
Distilled water	55.5

The same procedure was followed in preparing zinc glycinate crystals as in Example 1. One gram of zinc glycinate dissolved in distilled water deodorized 15 ml of titrated fatty acid solution from pH 8.0 to 7.0, below which a mild odour appears. Prior thereto, no odour was evident showing complete deodorization by zinc glycinate.

The addition of 1 gm glycine to 1 gm zinc glycinate in distilled water reduces the solution pH from 8.6 to 7.3. This combination is not as effective as zinc glycinate alone. The mixture deodorizes only 5 ml of fatty acid sweat solution. However, odour reduction is achieved from pH 7.3 to pH 6.5, below which some odour is present. Thus, no deodorizing properties can be attributed to glycine. As a matter of fact, the presence of free glycine reduces the deodorizing capacity of zinc glycinate.

Example 3

Components	*Amount (gms)*
Glycine	52.5
Zinc oxide	20.35
Distilled water	300.0

The above mixture was heated to 200°F (93°C) until a clear solution was obtained. 300 gms of absolute ethanol were added with mixing and a precipitate was formed. The mixture was filtered using #1 Whatman filter paper, and the crystals were washed several times with absolute ethanol. The white crystalline, non-hygroscopic precipitate was placed in a drying pan and air dried at 120°F (49°C)

overnight. The pH of a 1% aqueous solution was 8.3. The pH of a 7% saturated aqueous solution was 8.0. The zinc glycinate had a water solubility of about 6 gm/100 cc water.

A small quantity of a 1% aqueous zinc glycinate was added to synthetic sweat odour solution resulting in complete deodorization.

Example 4

Components	*Amount (gms)*
Glycine	15
Zinc carbonate	12.5
Distilled water	90

The glycine was dissolved in water and the zinc carbonate was added. CO_2 was liberated and the solution was evaporated to dryness to obtain white crystals of zinc glycinate which may be the monohydrate form of zinc glycinate. A 1% aqueous solution had a pH of 7.9. In lieu of evaporation, the solution may be spray dried to obtain the zinc glycinate crystals.

A 5% aqueous solution of the product, deodorizes a solution of artificial sweat.

Deodorant compositions

Example 5
Roll-on deodorant

Part 1 *Ingredient*	%
Deionized water	15.0
Propylene glycol	10.0
Hydroxyethyl cellulose	0.4

Part 2 *Ingredient*	%
SD 40 Ethanol	61.6
Zinc glycinate	10.0
Fumed silica	0.5

Part 3 *Ingredient*	%
Wheat germ glyceride	1.0
Polyoxypropylene stearylether	1.5

The ingredients listed under Part 1 were mixed, and preferably heated to 140°F (60°C) until a thick, uniform dispersion was formed. The ingredients listed under Part 2 were homogenized and added to the thick uniform mixture of Part 1 ingredients with mixing. The ingredients listed under Part 3 were admixed into the Part 1 and 2 mixture and preferably homogenized. A thick, stringy pituitous mixture was obtained which was placed in a conventional roll-on container.

This product was tested by adding 1 g of this roll-on product to 50 ml of a 5% aqueous synthetic human sweat solution. Total effective deodorizing was achieved in-vitro.

In-vivo testing consists in applying this product only to the right armpit, leaving the left armpit as a control. Underarm odour is rated after 24 and 48 hours.

Time	*Control arm*	*Test arm*
24 hrs.	slight odour	no odour
48 hrs.	moderate to heavy odour	no significant odour

Another in-vivo test consists in washing underarms but applying nothing in order to generate moderate odour under both armpits for about 24 hours. This roll-on product is applied to one armpit with almost instant deodorizing action. This product is applied to the second armpit with similar results.

The zinc glycinate product exhibited both odour prevention properties as well as neutralizing existing underarm odours.

No irritation was observed with the product on any occasions.

Aerosol deodorants

Part 1	*Example 6*	*Example 7*
Isopropyl palmitate	1.44	2.88
Bentone 38[1]	0.20	0.40
Propylene carbonate	0.06	0.12
Part 2		
Cyclomethicone	—	4.0
SD 40 Alcohol	5.0	—
Zinc glycinate powder	2.0	2.0
Perfume	0.1	0.1
Part 3		
Isobutane	91.2	90.5
	100.0	100.0

[1] Quaternium 18 hectorite

Procedure

The ingredients listed under Part 1 were combined and homogenized under high shear conditions to form a gel.

The part 1 gel was added to and mixed with the SD 40 alcohol or cyclomethicone, and the zinc glycinate powder and perfume were admixed. The slurry was placed in an aerosol container, crimped, and gassed with isobutane.

Both product sprays produce an invisible film on the skin, which afforded almost instant deodorization.

Example 8
Anhydrous deodorant cream

Part 1 *Ingredients*	%
Cyclomethicone	51.0
Isopropyl myristate	3.3882
Bentone 38	0.4706
Propylene carbonate	0.1412
Stearamide MEA (monoethanolamide)	1.5
Zinc stearate	1.5
Polyoxyethylene (20) isohexadecyl ether	2.0
Cocomonoethanolamide	3.0
Part 2 Zinc glycinate powder	10.0
Part 3 Dryflo starch (aluminium starch octenyl succinate)	25.0
Part 4 Colloidal silica	2.0

The ingredients listed under Part 1 were mixed and heated to 225°F (107°C) to form a translucent solution. The mixture was cooled to 180°F (82°C).

The zinc glycinate powder was admixed with Part 1 and the temperature was maintained at 150°F (66°C).

The starch was admixed with Parts 1 and 2 and the temperature was maintained at 150°F (66°C).

The colloidal silica was admixed with combined Parts 1, 2 and 3 while maintaining the temperature at 150°F (66°C).

The final mixture was poured into containers and allowed to cool. The mixture thickened, as it cooled to 100°F (38°C), into a non-pourable soft cream consistency.

The addition of this cream to a synthetic sweat solution effected complete deodorization almost instantaneously.

Known equivalents may be substituted for the specific ingredients in above compositions.

The zinc glycinate, both in the anhydrous form and in the monohydrate form has been found to be a highly effective deodorant in both preventing new odours and neutralizing existing odours, by chemical interaction with the odoriferous components. In addition, the zinc glycinate has been found to inhibit bacterial growth which further enhances its deodorancy properties by preventing bacteria multiplying and produce additional odoriferous components.

Claims

1. A deodorant composition comprising a solution or suspension of a particular deodorant active material which chemically neutralizes odoriferous compounds and inhibits bacterial growth, in a cosmetically acceptable vehicle, characterised in that the said deodorant active material is zinc glycinate.

2. A deodorant composition as claimed in Claim 1 in which the deodorant active material is anhydrous zinc glycinate.

3. A deodorant composition as claimed in Claim 1 in which the deodorant active material is the hydrated form of zinc glycinate.

4. A deodorant composition as claimed in Claim 1, 2 or 3 in which the deodorant active material constitutes about 1—50% by weight of the composition.

5. A deodorant composition as claimed in any one of Claims 1 to 4 which also contains a suspending or thickening agent and is dispensed from a roll-on container.

6. A deodorant composition as claimed in any one of Claims 1 to 4 in which the vehicle is in the form of a lotion comprising a liquid carrier of a lower alcohol or an aqueous alcoholic media.

7. A deodorant composition as claimed in Claim 6 which also contains non-volatile polar or non-polar ingredients selected from the group consisting of polyhydric alcohols and emollient oils.

8. A deodorant composition as claimed in any one of Claims 1 to 4 in which the vehicle is in the form of a stick comprising a monohydric or polyhydric alcohol gelled with a fatty alcohol or fatty amide or combination thereof.

9. A deodorant composition as claimed in any one of Claims 1 to 4 in which the vehicle is in the form of a cream comprising an aqueous emulsion of a fatty material.

10. A deodorant composition as claimed in any one of Claims 1 to 4 in which the zinc glycinate is suspended in a liquid vehicle comprising a carrier liquid and a liquified gaseous propellant, in the form of a deodorant spray.

11. A deodorant as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples 5 to 8.

12. A method of preparing zinc glycinate which comprises reacting an aqueous solution of glycine with zinc carbonate.

13. A method as claimed in Claim 13 in which the zinc glycinate is recovered in powdered form by evaporation of the solution or spray drying.

14. A method as claimed in Claim 12 substantially as specifically described herein with reference to Example 4.

15. Zinc glycinate whenever prepared by a method as claimed in any one of Claims 12 to 14.

16. A composition as claimed in any one of Claims 1 to 11 in which the zinc glycinate is as claimed in Claim 15.

17. A method of deodorizing odourous body locations comprising contacting said locations with a composition as claimed in any one of Claims 1 to 11 or Claim 16.

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(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

(72) Inventor: **Chatterjee, Ranjit (NMN)**
11041 Sycamore Grove Lane
Cincinnati, Ohio 45241(US)

(74) Representative: **Brooks, Maxim Courtney et al**
Procter & Gamble (NTC) Limited Whitley Road Longbenton
Newcastle-upon-Tyne NE12 9TS(GB)

(54) **Thiol heterocyclic deodorant composition and method of deodorization.**

(57) The present invention provides compositions containing a thiol heterocyclic compound and a topical carrier for topical application to the skin in the axilla or crotch region or to articles of clothing which are worn in the vicinity of such skin. The applicable deodorant agents comprise thiol heterocyclic compounds, or a pharmaceutically-acceptable salt thereof, comprising a heterocyclic ring structure having at least one heteroatom in the ring structure selected from the group consisting of oxygen, nitrogen, and sulfur; and wherein said heterocyclic ring structure has a least 1 thiol substituent attached to a carbon atom of said heterocyclic ring.

Methods for controlling malodor comprising depositing onto skin in the axilla or crotch region, or to articles of clothing worn in the vicinity of the skin of a safe and effective amount of a thiol heterocyclic deodorant agent of the present invention are also provided.

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TECHNICAL FIELD

The present invention related to compositions and methods for the treatment or prevention of malodor associated with human perspiration.

BACKGROUND OF THE INVENTION

Vast volumes of the chemical, medical and cosmetic literature have been generated concerning the causes, effects and prevention of human perspiration. "Perspiration", or "sweat", may be generally defined as including the excretion of the sweat glands situated in the corium or subcutaneous tissue, known as eccrine sweat glands, distributed over most of the body surface. While perspiration serves an important function in cooling the body through its evaporation, the by-products resulting from its bacterial degradation may be malodorous and aesthetically objectionable.

Malodor is particularly associated with perspiration secreted at areas of the body where apocrine sweat glands, in addition to eccrine sweat glands, can be found. Two principal areas which have apocrine sweat glands are the axilla and the crotch. See, for example, J. Labows, et al., "Perspectives on Axillary Odor", 34 J. Soc. Cosmetic Chemists 193-202 (1982) and P. Jackman, "Body Odor - The Role of Skin Bacteria" 1 Seminars in Dermatology 143-148 (1982). A variety of bacteria have been implicated in producing axillary malodor, a principal bacteria responsible for such malodor being the gram positive microflora naturally found in the axilla, e.g., the diphtheroids, such as the Corynebacteria and Propionibacteria, and the gram positive cocci, such as the Staphylococci and Micrococci.

A great number of compositions have been developed and described in the literature for reducing or eliminating the aesthetic problems associated with perspiration. See, for example, S. Plechner, "Antiperspirants and Deodorants", 2 Cosmetics, Science and Technology, 373-416 (M. Balsam and E. Sagarin ed. 1972). Such compositions can be generally classified as: antiperspirants, which serve to stop or reduce flow of perspiration; perfumes, which mask any objectionable odors resulting from perspiration; and deodorants, which stop or reduce the production of malodorous material in perspiration. For a variety of reasons, deodorant compositions are preferred by a large number of consumers. For example, some individuals are unable to use commercially-available antiperspirant products due to hypersensitivity to the astringent materials typically used in those products.

Deodorant compositions have primarily been thought of in the art in the context of stopping or reducing the formation of bacterial by-products in perspiration. This has been accomplished through the use of anti-microbial agents which attack the bacteria responsible for producing the malodorous by-products. While these anti-microbial deodorants have been effective in reducing malodor, they have not completely eliminated the formation of the malodorous condition. Thus, it is desirable to provide deodorant compositions which can further reduce malodor.

Additionally, it is desirable to reduce malodor once it is formed. In certain instances, malodor say remain, e.g., in the axilla and crotch areas, or in axilla and crotch areas of articles of clothing, even after washing. Traditionally, malodor that is already formed has been masked by perfumes. It is desirable to provide improved methods and compositions for reducing malodor that can remain subsequent to washing of the person or articles of clothing. In one approach, described in PCT International Patent Application Publication Number WO 87/04341, published July 30, 1987, it is disclosed that axillary malodor can be neutralized by the use of cupric sulfate, silver sulfate, potassium permanganate, ferric chloride, sodium hydroxide, silver proteinate, sodium hypochlorite, zinc sulfate, or copper gluconate. However, it is desirable to provide alternative technology for neutralizing malodor.

It is an object of this invention to provide compositions effective for controlling nonmicrobial malodor from human sweat. It is also an object of this invention to provide methods effective for controlling nonmicrobial malodor from human sweat.

SUMMARY OF THE INVENTION

The present invention provides compositions containing a thiol heterocyclic compound and a topical carrier for topical application to the skin in the axilla or crotch region or to articles of clothing which are worn in the vicinity of such skin. The applicable deodorant agents comprise thiol heterocyclic compounds, or a pharmaceutically-acceptable salt thereof, comprising a heterocyclic ring structure with from 5 to 10 heterocyclic ring atoms, wherein 1 to 3 of said ring atoms are selected from the group consisting of oxygen, nitrogen, and sulfur, and the remaining heterocyclic ring atoms being carbon atoms; and wherein said heterocyclic ring has at least 1 thiol substituent attached to a carbon atom of said heterocyclic ring.

DETAILED DESCRIPTION OF THE INVENTION

Although it has been suggested that malodor formation and neutralization may involve more than one mechanism, such mechanisms are not completely understood. Applicant has determined that even when perspiration from the axilla or crotch areas of humans is sterilized such that substantially no live bacteria remain to produce malodorous bacterial by-products, the perspiration can still develop aesthetically objectionable malodor. Such malodor shall hereinafter be referred to as "nonmicrobial malodor". Applicant has determined that certain vitamin B_6 compounds commonly secreted by humans from their eccrine sweat glands react when mixed with apocrine sweat gland secretions to form nonmicrobial malodor. Applicant has further determined that deodorant compositions containing certain thiol heterocyclic compounds are highly effective for reducing such nonmicrobial malodor in human perspiration. These compositions are particularly useful for controlling malodor in perspiration containing both apocrine and eccrine sweat. Furthermore, such compositions are effective for reducing nonmicrobial malodor rapidly after such odor is formed, or preventing nonmicrobial malodor.

Thiol heterocyclic compounds of the type described herein have been found to be highly effective for reducing the occurrence of the malodorous perspiration and, further, for deodorizing malodorous perspiration. Nonmicrobial malodor increases over time, especially when the rate of perspiration is high and when the time between washing is extended. It is believed that the concentration of nonmicrobial malodor precursors on the skin increases as additional perspiration is secreted and the aqueous component of previously secreted perspiration evaporates, thus increasing the formation of discernible nonmicrobial malodor. Without being limited by any theory, it is believed that thiol heterocyclic compounds react with the odor molecules produced from the interaction of the aldehyde form of vitamin B_6 (PLP) with sweat to reduce the volatility of the odorants and thereby reduce their ability to reach the human olfactory organ. The occurrence of such malodorous conditions from nonmicrobial sources can be substantially diminished by the thiol heterocyclic compounds of the present invention.

The compositions of the present invention comprise, as essential components, a thiol heterocyclic compound for controlling nonmicrobial malodor and a compatible carrier. As used herein, "controlling nonmicrobial malodor" means reducing previously formed nonmicrobial malodor to a less perceptable level to the human olfactory senses and/or inhibiting the occurrence of nonmicrobial malodor. As used herein, "compatible" means that none of the components of the carrier reacts with the thiol heterocyclic compound such that the ability of the composition to control nonmicrobial malodor is substantially impaired.

The term "alkyl", as used herein, means carbon-containing chains that are straight, branched or cyclic; and which are saturated, monounsaturated (i.e. one double or triple bond in the chain) or polyunsaturated (e.g. two or more double bonds in the chain; two or more triple bonds in the chain; one or more double and one or more triple bonds in the chain) which are substituted or unsubstituted. As used herein, saturated alkyl groups are referred to as "alkanyl"; unsaturated alkyl groups comprising double bonds bonds in the chain are referred to as "alkenyl"; and unsaturated alkyl groups comprising triple bonds in the chain are referred to as "alkynyl". The term "short chain alkyl", as used herein, means alkyls having from 1 to about 6 carbon atoms in the chain.

The term "aryl", as used herein, means aryl radicals which are substituted or unsubstituted. "Substituted aryl" means aryl radicals which have substituents on the aryl ring. Examples of aryls include phenyl, napthyl, and substituted phenyl or napthyl.

The term "substituted", as used herein, means mono- or polysubstituted, especially mono-, di- or trisubstituted. Examples of substitutents include halogen (especially fluorine, chlorine or bromine), alkyl, hydroxy, amino, aryl (especially phenyl or napthyl), carboxylate, nitro, $-CF_3$ and -OR wherein R is an unsubstituted alkyl group having from about 1 to about 3 carbon atoms (especially methoxy and ethoxy). Alkyl substituents are preferably C_1-C_6 alkyl, more preferably methyl or ethyl.

The deodorant agents of the present invention are thiol heterocyclic compounds wherein said compounds have a heterocyclic ring structure having at least one atom in the ring structure being a nitrogen, oxygen, or sulfur atom, and have a thiol substituent on the heterocyclic ring structure. As used herein, "heterocyclic ring structure" means a covalently bonded structure comprising a ring of from about 5 to about 8 atoms which may additionally comprise one or more other rings wherein all the rings are fused in the structure. As used herein "fused" rings are rings which have two or more ring atoms in common. The heterocyclic ring structures may be saturated, unsaturated or partially or wholly aromatic. Examples of heterocyclic ring structure compounds having oxygen, nitrogen, and sulfur ring atoms are found in CRC Handbook of Chemistry and Physics, 57th edition, Robert C. Weast, ed., CRC Press, Cleveland, Ohio, pp C-35 through C-58, incorporated by reference herein.

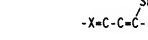
The heterocyclic ring structures of the deodorant agents of the present invention preferably contain from about 5 to about 10 ring atoms, more preferably 5 or 6 ring atoms. Also preferred is one to three atoms of said ring atoms being independently selected from the group consisting of oxygen, nitrogen, and sulfur; more preferred is one or two of said ring atoms being selected from the group consisting of oxygen, nitrogen, and sulfur; even more preferred is one to three of said ring atoms being nitrogen; even further preferred is one or two of said ring atoms being nitrogen; and the remainder of the ring atoms being carbon. In the heterocyclic ring structures, ring heteroatoms are not bonded directly to other ring heteroatoms. The nitrogen atom(s) of said ring structure are not directly bonded to an oxygen atom to form a N-oxide.

Compositions of the present invention comprise thiol heterocyclic compounds comprising a single ring or a plurality of fused rings; preferred is said thiol heterocyclic compound comprising a single heterocyclic ring structure having a thiol substituent or a heterocyclic ring structure having a thiol substituent located on any ring of such fused ring structure. Preferably, said thiol substituent on said fused ring structure is located on a heterocyclic ring. Preferred fused ring structures have two 5- or 6-membered rings.

The thiol heterocyclic compound may have a single thiol substituent or a plurality of thiol substituents. Preferably, the thiol heterocyclic compound has fewer than about four thiol substituents, preferably one or two thiol substituents, and most preferably, one thiol substituent.

The thiol substituted heterocyclic ring structure of the thiol heterocyclic deodorant agents of the present invention may be unsubstituted (other than the thiol substituent) or further substituted. Other substituents (other than the thiol) of said heterocyclic ring structure are preferably attached to the carbon atoms of said ring structure, and are preferably selected from the group consisting of hydroxy, amino, and substituted and unsubstituted alkyl. Preferred alkyls have from 1 to about 8 carbon atoms; more preferred alkyls are C_1-C_8 alkanyls and alkenyls. The nitrogen atom(s) of said heterocyclic ring structure may be substituted but are preferably unsubstituted.

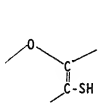
It is also preferable that at least one thiol substituent be attached to a carbon atom of a heterocyclic ring having a delocalized electron structure; examples of such carbon atoms include, but are not limited to, a carbon atom of a heteroaryl or aryl ring; a carbon atom of a heterocyclic ring that is double bonded to a nitrogen or sulfur atom of the heterocyclic ring; a carbon atom of a heterocyclic ring which is connected to a nitrogen or sulfur atom of the heterocyclic ring by conjugated double bonds; or a carbon atom of a heterocyclic ring which is either bonded to an oxygen atom of the heterocyclic ring or is double bonded to a carbon atom of the heterocyclic ring that is adjacent to an oxygen atom of the heterocyclic ring. "Connected to a nitrogen or sulfur atom by conjugated double bonds", as used above, means that the heterocyclic ring includes the following structural element:



wherein X is S or N.

The oxygen atom containing heterocyclic rings, as described above, include one of the following structural elements:

or



In addition to the thiol heterocyclic compounds described above, metal salts of such compounds are included in the compositions of the present invention. These include, but are not limited to, sodium, potassium, magnesium, zinc, aluminum, bismuth, and lithium salts of said compounds. Preferred are the above compounds, and their zinc, aluminum, and bismuth salts.

Preferred deodorant agents used in the composition of the present invention comprise thiol derivatives of the following classes of heterocyclic compounds: thiophenes, benzo[b]thiopenes, naphtha[2,3-6]-thiophenes, furans, pyrans, isobenzofurans, chromenes, pyrroles, imidazoles, pyrazoles, pyridines, pyrazines, pyrimidines, pyridazines, indolizines, isoindoles, indoles, purines, quinolizines, isoquinolines, quinolines, phthalazines, naphthyridines, quinoxalines, quinozolines, cinnolines, pteridines, oxazolines, isothiazoles, oxazoles, isoxazoles and furazans. Preferred classes of thiol derivative heterocyclic compounds include pyridines, pyrimidines, quinolines, and imidazoles. Especially preferred are imidazoles.

More preferred deodorant agents used in the composition of the present invention include thiol derivative heterocyclic compounds selected from the group consisting of 5,6 diamino-2-thiouracil, 1,5 diamino-6-hydroxy-2-mercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine, 2-mercaptopyrimidine, 2-thiouracil, 2,4-diamino-6-mercaptopyrimidine hemisulfate, ergothioneine, 2-thiohistidine, 2-mercaptopyridine, 4-mercaptopyridine, 2-mercaptobenzoxazole, 2-mercapto-6-nitrobenzothiazole, 2-thiocytosine, 6-thioxanthine, 2,6-dimercaptopyridine, 2-mercapto-5-nitropyridine, 2-mercaptoquinoline, 2-mercapto-4-hydroxy-6,8-dichloroquinazoline, 4-mercaptoquinazoline, 2-phenyl-4-quinazolinethiol, 3-amino-6-methyl-4-pyridazinethiol, 5-amino-4-pyridazinethiol, alpha-tocopherthiol, 2-amino-6,7-dimethyl-4-pteridinethiol, 4-mercaptopteridine, 2-mercapto-4-hydroxypteridine, and 2,4-diamino-6-phenyl-7-pteridinethiol.

Even more preferred thiol derivative heterocyclic compounds include 2-mercaptopyridine, 4-mercaptopyridine, 2-4-diamino-6-mercaptopyrimidine, 2-thiohistidine, and ergothioneine. Especially preferred are 2-thiohistidine and ergothioneine.

Thiol heterocyclic compounds applicable to this invention can be obtained commercially from industry chemical sources, such as Sigma Chemical Company (St. Louis, Missouri), Aldrich Chemical Company (Milwaukee, Wisconsin), K&K Laboratories (Plainview, New York), and P&B Research Chemicals (Waterbury, Connecticut).

It is preferable that the thiol heterocyclic deodorant agents not react with components found in perspiration in such a way that would cause the thiol heterocyclic compound to become discernibly malodorous, or which would significantly reduce its effectiveness. However, perfumes can be added to the compositions, as optional ingredients, to mask slight malodors of the thiol heterocyclic deodorant agent and its reaction products.

The compositions of the present invention comprise a safe and effective amount of a thiol heterocyclic compound when used as intended. As used herein, a "safe and effective amount" is an amount which is effective for eliminating or substantially reducing nonmicrobial malodor, while being safe for the intended use at a reasonable benefit/risk ratio.

A. Topical Compositions

One aspect of the present invention is deodorant compositions which comprise a thiol heterocyclic compound and a topical carrier. The deodorant compositions of the present invention comprising a thiol heterocyclic compound can be a variety of products which, in ordinary use, are applied topically to the skin or are applied to articles of clothing which are worn in the vicinity of the skin. Compositions formulated for topical application to skin, or prepared for deposition upon articles of clothing and intended to at least initially remain deposited at the time that the article is worn, comprise a safe and effective amount of the thiol heterocyclic compound and a topical carrier for depositing or releasing the deodorant agent. As used herein "applied to the skin" and "application to the skin" include deposit on the skin such that the deodorant agent can remain on the skin subsequent to the typical use of the composition as well as treatment of the skin with the composition wherein the deodorant agent is typically not deposited, e.g., skin cleaning compositions (discussed in more detail below) which are typically rinsed off subsequent to use.

The topical carriers of the deodorant compositions of the present invention can be in the form of liquids, solids, creams, gels, lotions, or other forms, and are preferably formulated to deposit the deodorant agent on the skin or article of clothing. As used herein, "deposited" and "deposit" of the deodorant agent on the skin means application of a deodorant composition to the skin such that the deodorant agent can remain on the skin subsequent to the typical use of the deodorant composition, including conventional post-deodorant composition application steps, if any. Such topical carriers include, but are not limited to, those formulated

as conventional deodorant compositions such as creams, sticks, roll-on liquids and spray liquids (including aerosols); body lotions, creams and oils, such as skin lotions, skin conditioners, sun and wind screens, and sun tanning lotions and oils; and skin cleansing products such as bar soaps, liquid soaps and cleaning gels.

Typically, topical deodorant compositions of the present invention contain from about 0.01% to about 20% of the thiol heterocyclic deodorant agent, preferably from about 0.05% to about 5%, more preferably from about 0.5% to about 2%.

Preferred deodorant compositions of the present invention are conventional deodorant compositions, including anti-perspirant/deodorant compositions, formulated for topical application to the axilla area of the body, or for application to the crotch area. The specific components to be included in the deodorant compositions of the present invention depend upon the particular mode of application that is desired. These methods of application, as well as the components that may be used in such compositions are well known in the art. Many such compositions are described in S. Plechner, "Antiperspirants and Deodorants" 2 Cosmetics, Science and Technology, 373-416 (M. Balsam and E. Sagarin ed. 1972), incorporated by reference herein.

A topical carrier for deodorant compositions formulated primarily for deposit of the thiol heterocyclic deodorant agent on the skin in the axilla area for malodor control is preferably hydrophobic, with less than about 5% water, more preferably less than about 2% water, and most preferably with essentially zero percent water. Other compositions may contain high amounts of water, for the presence of water is not believed to affect the efficacy of the thiol heterocyclic deodorant agent.

Topical carriers useful for depositing the thiol heterocyclic deodorant agents to skin in the form of creams, ointments, lotions, oil-in-water and water-in-oil emulsions are known in the art, and include, for example, the water-in-oil emulsions disclosed in U.S. Patent 4,254,105, Fakuda et al., issued March 3, 1981 (incorporated by reference herein), and triple emulsion carrier systems such as the oil-in-water-in-silicone fluid emulsions as disclosed in European Patent Specification 281,394, Figueroa et al., published September 7, 1988 (incorporated by reference herein).

1. Liquids

Liquid compositions useful herein, such as roll-ons, sprays, and aerosols, preferably contain a liquid emollient as all or a substantial part of the topical carrier. Such compositions are suitable for delivery (respectively) from conventional roll-on, spray and aerosol containers known in the art. Such emollients include fatty acid and fatty alcohol esters, water-insoluble ethers and alcohols, polyorganosilicones, and mixtures thereof. Polyorganosilicones are among the preferred emollients useful herein. Liquid topical carriers are disclosed in the following patent documents, incorporated by reference herein: U.S. Patent 4,053,851, Pader, et al., October 11, 1977; U.S. Patent 4,065,564, Miles, Jr., et al., issued December 27, 1977; U.S. Patent 4,073,880, Pader, et al., issued February 14, 1978; U.S. Patent 4,278,655, Elmi, issued July 14, 1981; British Patent Application 2,018,590, Elmi, et al., published October 24, 1979; and European Patent Specification 28,853, Beckmeyer, et al., issued July 11, 1984.

The liquid deodorant compositions of the present invention may also contain an alcohol and/or a polyol as a substantial component in the topical carrier. Alcohols useful herein include ethanol, propanol, isopropanol, and mixtures thereof. Polyols useful herein include glycols such as propylene glycol. The present liquid compositions may also contain a bulking agent to modify the physical and/or cosmetic characteristics of the composition. Such bulking agents are typically present at a level of from about 1% to about 8%. Bulking agents useful herein include talc, colloidal silicas, clays, and mixtures thereof.

2. Aerosols

Aersol compositions of the present invention contain one or more volatile materials, herein "aerosol propellants", which in a gaseous state carry the other components of the present invention. The aerosol propellants useful herein typically have a boiling point within the range of from about -45 °C to about 5 °C. The aerosol propellants are liquified when packaged in conventional aerosol containers under pressure. The rapid boiling of the aerosol propellant upon leaving the aerosol container aids in the atomization of the other components of the aerosol compositions.

Aerosol propellants useful herein include those well known in the art. Such aerosol propellants include the chemically-inert hydrocarbons such as propane, n-butane, isobutane, cyclopropane and mixtures thereof, as well as halogenated hydrocarbons such as dichloro difluoromethane (propellant 12), 1,1-dichlor-1,1,2,2tetrafluoroethane (propellant 114), 1-chloro-1,1-difluoro-2,2trifluoroethane (propellant 115), 1-chloro-

1,1-difluoroethylene (propellant 142B), 1,1-difluoroethane (propellant 152A), monochlorodifluoromethane, and mixtures thereof. Isobutane, used singly or admixed with other hydrocarbons, is preferred for use in aerosol compositions of the present invention.

3. Deodorant Sticks

Solid compositions of the present invention, as in a stick form known in the art, typically comprise a liquid base material and a solidifying agent. These deodorant sticks can generally be described as being either gel sticks or wax sticks, depending upon the particular liquid base materials and solidifying agents used. In general, liquid base materials are present at a level of from about 10% to about 97%. The solidifying agent is typically present at a level of from about 1% to about 7%.

As is appreciated by those skilled in the art, the selection of a particular liquid base material, as well as the selection of a suitable solidifying agent, will vary depending upon the particular type and rheology of deodorant stick desired. A variety of liquid base materials and solidifying agents among those useful herein, as well as sticks made from these materials, are described in the following documents, all incorporated by reference herein: S. Plechner, "Antiperspirants and Deodorants", 2 Cosmetics, Science and Technology, 373-416 (M. Balsam and E. Sagarin ed. 1972); C. Fox "Gel and Sticks Review and Update", 99 Cosmetics & Toiletries 19-52 (1984); N. Geria, "Formulation of Stick Antiperspirants and Deodorants", 99 Cosmetics & Toiletries, 55-99 (1984); and "Gels and Sticks Formulary", 99 Cosmetics & Toiletries, 77-87 (1984).

The liquid base materials used in wax deodorant sticks generally also serve as emollients, improving the cosmetic acceptability of the deodorant sticks. Such emollient materials include fatty acid and fatty alcohol esters, water-insoluble ethers and alcohols, polyorganosiloxanes, and mixtures thereof. Polyorganosiloxanes are among the preferred liquid base materials useful in wax deodorant sticks of the present invention.

Solidifying agents useful in wax deodorant sticks of the present invention are waxy materials typically incorporated at a level of from about 5% to about 50%. Among such waxy materials useful herein are the high melting point waxes, having a melting point of from about 62 °C to 102 °C. Lower melting point waxes having a melting point of from about 37 °C to 75 °C are preferred. Such low-melting point waxes include fatty acids, fatty alcohols, fatty acid esters and fatty acid amides, and mixtures thereof. Stearyl alcohol, cetyl alcohol, and mixtures thereof are among the particularly preferred waxy materials useful in the deodorant stick compositions of the present invention. Liquid base materials and solidifying agents among those useful in the wax-type deodorant sticks of this invention are disclosed in the following U.S. Patents, incorporated by reference herein: U.S. Patent 4,049,792, Elsnau, issued September 20, 1977; U.S. Patent 4,151,272, Geary, et al., issued April 24, 1979; U.S. Patent 4,299,432, Geria, issued October 21, 1980; U.S. Patent 4,280,994, Turney, issued July 28, 1981; U.S. Patent 4,126,679, Davy, et al., issued November 21, 1978; and European Patent Specification 117,070, May, published August 29, 1984.

Gel deodorant sticks of the present invention contain liquid base material which may be selected so as to also provide desirable cosmetics, such as emolliency and/or a cooling sensation when applied to the skin. Liquid base materials useful in such gel sticks include water, lower monohydric alcohols, polyhydric alcohols, and mixtures thereof. Among such materials are ethanol, isopropanol, n-propanol, n-butanol, i-butanol, t-butanol, ethylene glycol, propylene glycol, trimethylene glycol, glycerine, 1,3-butanediol, 1,4-butanediol, and mixtures thereof. Ethanol, propylene glycol, and mixtures thereof are preferred liquid base materials for use in gel sticks of this invention.

Solidifying agents useful in gel deodorant sticks of this invention are, in general, surface-active compounds which form networks immobilizing or solidifying the liquid base materials into a gel. Such solidifying agents typically include soaps, higher fatty acid amides of alkyl amines, benzylidene sorbitols, propionates and lactates, waxes, and mixtures thereof. Preferable solidifying agents in gel deodorant sticks of the present invention are nonionic in character. Among the preferred solidifying agents useful in the gel deodorant sticks of this invention are the benzylidene sorbitols, in particular the dibenzaldehyde monosorbitol acetals. Such materials are available from a variety of sources, e.g., Gell All-D™ (manufactured by New Japan Chemical Company, Ltd.) and Millithix™ (Manufactured by Milliken Chemical, Division of Milliken & Company). Liquid base materials and solidifying agents among those useful in the gel-type deodorant sticks of this invention are disclosed in the following patent documents, all incorporated by reference herein: U.S. Patent 2,900,306, Slater, issued August 18, 1959; U.S. Patent 3,255,082, Barton, Issued June 7, 1966; U.S. Patent 4,137,306, Rubino, et al., issued January 30, 1979; U.S. Patent 4,154,816, Roehl, et al., issued May 15, 1979; U.S. Patent 4,226,889, Yuhas, issued October 7, 1980; U.S. Patent 4,346,079, Roehl, issued August 24, 1982; U.S. Patent 4,383,988, Teng, et al., issued May 17, 1983; U.S. Patent 4,504,465, Sampson et al., issued Marcy 12, 1985; and European Patent Specification 107,330,

Luebbe, et al., published May 2, 1984; and U.S. Patent 4,816,261, Luebbe et al, issued 1989. Preferred gel sticks, incorporating benzylidene sorbitols and cetyl alcohol, are described in U.S. Patent No. 4,743,444, McCall, issued May 10, 1988 (incorporated by reference herein).

The deodorant sticks of the present invention, particularly the wax-type deodorant sticks, may contain inert filler materials. Such materials include talc, colloidal silica (such as Cab-O-Sil®, sold by Cabot Corporation), clays (such as bentonites) and mixtures thereof. Such filler materials are described in U.S. Patent 4,126,679, Davy, et al., issued November 21, 1978 (incorporated by reference herein) and European Patent Specification 117,070, May, published August 29, 1984 (incorporated by reference herein).

The deodorant compositions of the present invention for topical application to skin may also contain optional components which serve as additional "active" components when deposited on the skin in addition to the thiol heterocyclic deodorant agents of the present invention. Such additional active components preferably do not, however, substantially interfere with the deodorant activity of thiol heterocyclic. Active components include, but are not limited to, other deodorant agents, such as anti-microbial agents, e.g. bacteriocides and fungicides, and antiperspirant agents. The active components must be stable in the formulations of the present compositions. A "safe and effective" amount of an active component is preferably used. Various active components among those useful in this invention are described in U.S. Patent 4,226,889, Yuhas, issued October 7, 1980 (incorporated by reference herein).

Preferred antiperspirant materials useful in the deodorant compositions of this invention include aluminum and zirconium salts, such as aluminum halides, aluminum hydroxy halides, zirconyl oxide halides, zirconyl hydroxy halides, and mixtures thereof. Antiperspirant materials among those useful herein are described in European Patent Specification 28,853, Beckmeyer, et al., published July 11, 1984 (incorporated by reference herein). Such materials are typically included at levels of from about 15% to about 40%; based upon the total weight of the composition.

Other optional antiperspirant materials include antihistamines selected from the group of ethanolamines, ethylenediamines, alkylamines, phenothiazines, and piperazines, or pharmaceutically acceptable salts thereof, as described in U.S. Patent 4,226,850, Packman, issued October 7, 1980 and U.S. Patent 4,234,566, Packman, issued November 18, 1980 (both incorporated by reference herein). Still other optional antiperspirant materials include various anticholinergic agents, such as esters of the Belladonna alkaloids scopolamine and atropine, as disclosed in U.S. Patent 3,312,709, MacMillan, issued April 4, 1967, U.S. Patent 3,326,768, MacMillan, issued June 20, 1967, U.S. Patent 3,767,786, MacMillan, issued October 23, 1973, and U.S. Patent 3,624,200, Moffett, issued November 1971 (all incorporated by reference herein).

As is appreciated by those skilled in the art, certain of the antiperspirant materials described above may be ineffective in, or lead to instability of, compositions of this invention. Accordingly, compositions of this invention may contain a buffering agent so as to maintain a pH of at least about 6.0 in the composition. Such buffering agents are described in U.S. Patent 4,154,816, Roehl, et al., issued May 15, 1979, U.S. Patent 4,346,079, Roehl, issued August 24, 1982; and U.S. Patent 4,518,582, Schamper, et al., issued May 21, 1985 (all incorporated by reference herein).

Among the preferred compositions of the present invention are those which also include a safe and effective amount of deodorant agents other than the thiol heterocyclic deodorant agent, such as antimicrobial agents (e.g. bacteriocides and fungicides), or mixtures thereof. Such other deodorant agents are usually present at levels of from about 0.1% to 10% (by weight of the composition). Suitable other deodorant agents include bacteriostatic quaternary ammonium compounds such as cetyl-trimethyl ammonium bromide, cetyl pyridinium chloride, benzethonium chloride, diisobutyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, sodium N-lauryl-sarcosine, sodium N-polymethyl sarcosine, lauroyl sarcosine, N-myristoyl glycine, potassium N-lauroyl sarcosine, stearyl trimethyl ammonium chloride, and mixtures thereof. Other suitable deodorant agents include 2,4,4'-trichloro-2'hydroxydiphenyl ether, zinc pyrithione (ZPT), and sodium bicarbonate. Particularly preferred other deodorant agents include a diaminoalkyl amide, such as L-lysine hexadecyl amide, as disclosed in U.S. Patent 3,574,747, Denning, issued April 13, 1971 (incorporated by reference herein).

Other optional components of the deodorant compositions of the present invention include perfumes, pigments, dyes, colorants, and ultraviolet absorbers.

The deodorant compositions of the present invention may be made by a variety of techniques well know in the art. For example, such techniques for making solid deodorant compositions are described in "Gels and Sticks Formulary", 99 Cosmetics & Toiletries 77-87 (1984), incorporated by reference herein.

4. Creams, Ointments and Lotions

Creams, ointments, and lotion composition of the present invention typically comprise one or more emollients as components of the topical carriers. As used herein, "emollients" refer to materials used for the prevention or relief of dryness, as well as for the protection of the skin. A wide variety of suitable emollients are known and may be used herein. Sagarin, Cosmetics, Science and Technology, 2nd Edition, Vol. 1, pp. 32-43 (1972), incorporated herein by reference, contains numerous examples of suitable materials. Examples of classes of useful emollients include the following:

Hydrocarbon oils and waxes; silicone oils, such as dimethyl polysiloxanes, methylphenyl polysiloxanes, water-soluble and alcohol-soluble silicone glycol copolymers; triglyceride esters, for example vegetable and animal fats and oils; acetoglyceride esters, such as acetylated monoglycerides; ethoxylated glycerides, such as ethoxylated glyceryl monostearate; alkyl esters of fatty acids having 10 to 20 carbon atoms; alkenyl esters of fatty acids having 10 to 20 carbon atoms; fatty acids having 10 to 20 carbon atoms; fatty alcohols having 10 to 20 carbon atoms; fatty alcohol ethers; ether-esters such as fatty acid esters of ethoxylated fatty alcohols; lanolin and derivatives; polyhydric alcohols and polyether derivatives; polyhydric alcohol esters; wax esters such as beeswax, spermaceti, myristyl myristate, stearyl stearate; beeswax derivatives; vegetable waxes including carnauba and candelilla waxes; phospholipids, such as lecithin and derivatives; sterols such as cholesterol and cholesterol fatty acid esters; and amides such as fatty acid amides, ethoxylated fatty acid amides, solid fatty acid alkanolamides.

Particularly useful emollients which provide skin conditioning are glycerol, hexanetriol, butanetriol, lactic acid and its salts, urea, pyrrolidone carboxylic acid and its salts, amino acids, guanidine, diglycerol and triglycerol.

A lotion of the present invention in the form of a solution typically comprises from about 0.01% to about 20%, preferably from about 0.1% to about 5%, of a thiol heterocyclic deodorant agent; from about 1% to about 20%, preferably from about 5% to about 10%, of an emollient; and from about 50% to about 90%, preferably from about 60% to about 80%, water. A cream of the present invention in the form of a solution typically comprises from about 0.01% to about 20%, preferably from about 0.1% to about 5%, of a thiol heterocyclic deodorant agent; from about 5% to about 50%, preferably from about 10% to about 20%, of an emollient, and from about 45% to about 85%, preferably from about 50% to about 75%, water.

An ointment of the present invention may comprise a simple base of animal or vegetable oils or semi-solid hydrocarbons (oleaginous). Ointments may also comprise absorption ointment bases which absorb water to form emulsions. Examples of such ointment bases include anhydrous lanolin and hydrophilic petrolatum. Emulsion ointment bases may be oil-in-water or water-in-oil emulsions. Ointment carriers may also be water soluble. Examples of such ointment carriers include components such as glycolethers, propylene glycols, polyoxyl stearates, and polysorbates. An ointment typically comprises from about 2% to about 10% of an emollient plus from about 0.1% to about 2% of a thickening agent. A more complete disclosure of thickening agents useful herein can be found in Segarin, Cosmetics, Science and Technology, 2nd Edition, Vol. 1, pp. 72-73 (1972), incorporated herein by reference.

If a topical carrier of the present invention is formulated as an emulsion, typically from about 1% to about 10%, preferably from about 2% to about 5%, of the carrier comprises an emulsifier. Emulsifiers may be nonionic, anionic or cationic. Suitable emulsifiers are disclosed in, for example, U.S. Patent 3,755,560, issued August 28, 1973, Dickert et al.; U.S. Patent 4,421,769, issued December 20, 1983, Dixon et al.; and McCutcheon's Detergents and Emulsifiers, North American Edition, pages 317-324 (1986); the disclosures of which are incorporated herein by reference. Preferred emulsifiers are anionic or nonionic, although the other types may also be used.

Single emulsion skin care preparations, such as lotions and creams, of the oil-in-water type and water-in-oil type are well-known in the cosmetic art and are useful in the present invention. Multiphase emulsion compositions, such as the water-in-oil-in-water type, as disclosed in U.S. Patent No. 4,254,105, Fakuda et al., issued March 3, 1981, herein incorporated by reference, are also useful in the present invention. In general, such single or multiphase emulsions contain water, emollients and emulsifiers as essential ingredients.

Triple emulsion carriers comprising an oil-in-water-in-silicone fluid emulsion composition as disclosed in European Patent Specification 281,394 (supra) are also useful in the present invention. More particularly, such triple emulsion carrier systems comprise a) from about 15% to about 90% by weight (of the vehicle) of a silicone fluid continuous phase consisting essentially of at least one liquid organopolysiloxane, b) from about 30% to about 80% by weight (of the vehicle) of an aqueous discontinuous phase comprising an oil-in-

water emulsion of a cosmetically-acceptable oily liquid non-particulate phase dispersed in an aqueous phase and c) from about 0.5% to about 5% by weight (of the vehicle) of an effective dispersing amount of dimethicone copolyol for dispersing (b) in (a).

Another emulsion carrier useful in the compositions of the present invention is a micro-emulsion carrier. Such a carrier comprises from about 9% to about 15% squalane; from about 25% to about 40% silicone oil; from about 8% to about 20% of a fatty alcohol; from about 15% to about 30% of polyoxyethylene sorbitan mono-fatty acid (commercially available under the trade name Tweens®) or other nonionics; and from about 7% to about 20% water.

Lotions and creams can be formulated as emulsions as well as solutions. Typically such lotions in the form of emulsions comprise from about 0.01% to about 20%, preferably from about 0.1% to about 5%, of a thiol heterocyclic deodorant agent from about 1% to about 20%, preferably from about 5% to about 10%, of an emollient; from about 25% to about 75%, preferably from about 45% to about 95%, water; and from about 1% to about 10%, preferably from about 2% to about 5%, of an emulsifier. Such creams in the form of emulsions typically comprise from about 0.01% to about 20%, preferably from about 0.1% to about 5%, of a thiol heterocyclic deodorant agent; from about 1% to about 20%, preferably from about 5% to about 10%, of an emollient; from about 20% to about 80%, preferably from about 30% to about 70%, water; and from about 1% to about 10%, preferably from about 2% to about 5%, of an emulsifier.

5. Skin Cleansing

In addition to the deodorant compositions described above, the deodorant compositions of the present invention include skin cleansing deodorant compositions, which comprise a thiol heterocyclic compound and a topical carrier which includes a safe and effective surfactant for topical application to human skin. The term "safe and effective surfactant for topical application to human skin" refers to a surfactant which is not only an effective skin cleanser, but also can be used without undue toxicity, irritation, allergic response, and the like. The skin cleansing deodorant compositions of the present invention preferably contain from about 0.01% to about 20% of the thiol heterocyclic deodorant agent and from about 1% to about 90%, preferably from about 50% to about 90%, of a surfactant for topical application to human skin.

The physical form of the skin cleansing, deodorant compositions is not critical. The compositions can be, for example, formulated as toilet bars, liquids, pastes, or mousses. Toilet bars are most preferred since this is the form of cleansing agent most commonly used to wash the skin.

Those skilled in the art will recognize that active ingredients applied to skin from skin cleansing compositions may not significantly deposit on the skin due to factors such as rinsing which typically follows the application of such products. Even when significant deposit of the thiol heterocyclic on the skin is not attained, the compositions can still be highly effective for controlling nonmicrobial malodor that was previously formed in the axilla or crotch areas. Controlling nonmicrobial malodor in connection with skin cleaning compositions is especially of great benefit since malodorous skin condition can remain even after the affected axilla and crotch areas are washed with conventional skin cleansing compositions.

Any safe and effective surfactant which is compatible with the thiol heterocyclic deodorant agent can be used in the compositions of the present invention, including surfactants selected from anionic, nonionic, zwitterionic, amphoteric and ampholytic surfactants, as well as mixtures of these surfactants. Such surfactants are well-known to those skilled in the detergency art. Suitable surfactants can be found, for example, in McCutcheon's Detergents and Emulsifiers, North American Ed. pages 317-324 (1986), incorporated herein by reference. The particular surfactant is not believed to be critical to obtaining the anti-nonmicrobial malodor benefits of the present invention.

The skin cleansing deodorant compositions of the present invention can optionally contain, at their art-established levels, materials which are conventionally used in skin cleansing compositions, including antibacterial agents and fungicides, including those described above and also those described in U.S. Patent 3,256,200, Reller et al., issued June 14, 1966 (incorporated by reference herein); emollients, such as those described above, and also including mineral oils, paraffin wax having a melting point of from about 100°F to about 170°F, fatty sorbitan esters (see U.S. Patent 3,988,255, Seiden, issued October 26, 1976, incorporated by reference herein), lanolin and lanolin derivatives, esters such as isopropyl myristate and triglycerides such as coconut oil or hydrogenated tallow; free fatty acid, such as coconut oil fatty acid, preferably at levels up to about 10%, to improve the volume and quality (creaminess) of the lather produced by the compositions; and other ingredients such as perfumes, dyes, pigments, polymeric skin feel aids (such as cationic quaternized guar gum, e.g., Jaguar C-14-S, from Hoechst Celanese Corp.), humectants, thickening agents, preservatives, alkaline agents, propoxylated glycerol derivative skin conditioning agents, or other cosmetic adjuvants.

Skin cleansing compositions formulated as toilet soap bars generally comprise from about 50% to about 90% surfactant. Moisture is generally present at levels of from about 5% to about 20%. Skin cleansing compositions formulated as liquids generally comprise from about 10% to about 30% surfactant and from about 60% to about 90% water. Skin cleansing compositions formulated as pastes generally comprise from about 20% to about 60% surfactant and from about 30% to about 50% water. Pastes and liquids will also generally contain organic thickening agents such as natural gums and polymers.

Examples of soap-based toilet bar compositions are found in U.S. Patent 3,567,749, Megson et al., issued April 27, 1971, incorporated herein by reference. Examples of synthetic-based toilet bars which can be used in preparing compositions of the present invention are found in U.S. Patent 2,987,484, Lundberg et al., issued June 6, 1961, incorporated by reference herein. Other examples of soap/synthetic-based toilet bars are found in U.S. Patent 3,070,547, Chaffee, issued December 25, 1962 and U.S. Patent 3,376,229, Haas et al., issued April 2, 1967, incorporated herein by reference. Examples of soap-based liquid cleansing compositions which can be used in preparing liquid compositions of the present invention are found in U.S. Patent 4,310,433, Stiros, issued January 12, 1982, incorporated herein by reference. Examples of synthetic-based liquid cleansing compositions which can be used in preparing compositions of the present invention are found In U.S. Patents 4,338,211, Stiros, issued June 6, 1982, incorporated herein by reference. Paste compositions can be made by appropriate reduction in the levels of water in the compositions of U.S. Patents 4,310,433 and 4,338,211, incorporated by reference herein. Examples of ultra mild skin cleansing compositions which can be used in preparing compositions of the present invention can be found in U.S. Patent 4,673,525, Small et al., issued June 16, 1987, incorporated by reference herein. Examples of skin cleansing mousse compositions with ethoxylated nonionic and wholly or partially esterified polyol nonionic surfactants and also having skin conditioning ingredients such as emollients and skin moisturizers can be found in U.S. Patent 4,708,813, Snyder, issued November 14, 1987, incorporated by reference herein. In addition to disclosing examples of skin cleansing compositions of the present invention, the above incorporated patents also disclose a variety of surfactants that can be used in the compositions of the present invention, including both soap-based and synthetic detergent-based surfactants. Skin cleansing deodorant compositions of the present invention are made by incorporating a thiol heterocyclic deodorant agent in the above-identified compositions.

B. Laundry Product Compositions

Another aspect of the present invention involves laundry product compositions comprising a thiol heterocyclic deodorant agent of the present invention and a laundry product carrier. Laundry product carriers can be in liquid, granular, or solid form and include liquid and granular detergents, and wash-added, rinse-added and dryer-added substrates which may also contain other ingredients, such as fabric conditioning and/or detergent ingredients. The laundry product compositions are formulated such that the thiol heterocyclic deodorant agent either deodorizes the article of clothing during the laundry step and is washed or rinsed off (removal of odor), or is deposited on the article of clothing and remains to control nonmicrobial malodor (prevention of odor). The laundry product compositions of the present invention are believed to be especially beneficial for reducing nonmicrobial malodorous substances that become absorbed into the fabric.

Typically such laundry product compositions comprise from about 0.001% to about 20% of a thiol heterocyclic deodorant agent. Laundry product compositions formulated for removal of odor preferably comprise from about 0.001% to about 1% of a thiol heterocyclic deodorant agent, more preferably from about 0.005% to about 0.5%, more preferably still from about 0.01% to about 0.1%. Laundry product compositions formulated for prevention of odor preferably comprise from about .01% to about 10% of a thiol heterocyclic deodorant agnet, more preferably from about 0.1% to about 5%.

"Laundry product compositions", as used herein, include such compositions as liquid and granular laundry detergents, liquid and granular fabric conditioning and washer or dryer added substrates also containing fabric conditioners and/or detergent ingredients. Such compositions comprise a thiol heterocyclic agents of the present invention and typically comprise, one or more of the following components.

Detersive Surfactants: The detergent compositions of this invention will contain organic surface-active agents ("surfactants") to provide the usual cleaning benefits associated with the use of such products.

Detersive surfactants useful herein include well-known synthetic anionic, nonionic, amphoteric and zwitterionic surfactants. Typical of these are the alkyl benzene sulfonates, alkul- and alkylether sulfates, paraffin sulfonates, olefin sulfonates, amine oxides, alpha-sulfonates of fatty acids and of fatty acid esters, alkyl glycosides, ethoxylated alcohols and ethoxylated alkyl phenols, and the like, which are well-known from the detergency art. In general, such detersive surfactants contain an alkyl group in the C_9-C_{18} range;

the anionic detersive surfactants can be used in the form of their sodium, potassium or triethanolammonium salts. Standard texts such as the McCutcheon's Index contain detailed listings of such typical detersive surfactants. C_{11}-C_{14} alkyl benzene sulfonates, C_{12}-C_{18} paraffin-sulfonates, and C_{11}-C_{18} alkyl sulfates and alkyl ether sulfates are especially preferred in the compositions of the present type.

Also useful herein are the water-soluble soaps, e.g., the common sodium and potassium coconut or tallow soaps well-known in the art. Unsaturated soaps such as alkyl soaps may be used, especially in liquid formulations. Saturated or unsaturated C_9-C_{15} hydrocarbyl succinates are also effective.

Mixtures of the anionics, such as the alkylbenzene sulfonates, alkyl sulfates and paraffin sulfonates, with C_9-C_{16} ethoxylated alcohol surfactants are preferred for through-the-wash cleansing of a broad spectrum of soils and stains from fabric.

Combinations of anionic, cationic and nonionic surfactants can generally be used. Such combinations, or combinations only of anionic and nonionic surfactants, are preferred for liquid detergent compositions. Such surfactants are often used in acid form and neutralized during preparation of the liquid detergent composition. Preferred anionic surfactants for liquid detergent compositions include linear alkyl benzene sulfonates, alkyl sulfates, and alkyl ethoxylated sulfates. Preferred nonionic surfactants include alkyl polyethoxylated alcohols.

Anionic surfactants are preferred for use as detergent surfactants in granular detergent compositions. Preferred anionic surfactants include linear alkyl benzene sulfonates and alkyl sulfates. Combinations of anionic and nonionic detersive surfactants are especially useful for granular detergent applications.

Detergent compositions will typically contain from about 10% to about 60% of a water-soluble detergent surfactant. Suitable surfactants and detergent compositions are described in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975 and U.S. Patent 4,294,710, Hardy et al., issued October 13, 1981, both of which are incorporated herein by reference.

Conventional Builders: Builders used in the practice of this invention include various metal ion sequestering agents such as amine chelants and phosphonate chelants, such as diethylenetriamine pentaacetates, the alkylene amino phosphonates such as ethylenediamine tetraphosphonate, and the tripolyphosphate and "pyro" builders well known in the art. Importantly, various nonphosphorus builders can be used. Included among these by way of exemplification, but not limitation, are: 1-10 micron Zeolite A; 2,2'-oxodisuccinate; tartrate mono- and di-succinates; citrates; C_9-C_{14} hydrocarbyl succinates; sodium carbonate; and mixtures thereof. Inorganic salts such as sodium sulfate can also be present. Lists of builders useful herein can be had by reference to U. S. Patent 4,704,233, cited above.

Bleaches: Various well-known bleaching agents (especially fiber and fabric bleaches) are well known and may be used as components of the laundry product carriers. For laundry products, the sodium perborate mono- and tetra-hydrates are preferred, although the percarbonates and persulfates are also useful. Aqueous hypochlorite is also a routine additive in many laundering operations. As noted previously, bleaching agents useful as components of the compositions of the present invention are limited to those which are compatible with the thiol heterocyclic compound in the composition.

Detersive Adjuncts: The compositions herein can contain various ingredients which aid in their cleaning performance. For example, it is preferred that the laundry compositions herein also contain enzymes to enhance their through-the-wash cleaning performance on a variety of soils and stains. Amylase and protease enzymes suitable for use in detergents are well-known in the art and in commercially available liquid and granular detergents. Commercial detersive enzymes (preferably a mixture of amylase and protease) are typically used at levels of 0.001% to 2%, and higher, in the present compositions.

Moreover, the compositions herein can contain, in addition to ingredients already mentioned, various other optional ingredients typically used in commercial products to provide aesthetic or additional product performance benefits. Typical ingredients include pH regulants, perfumes, dyes, bleaches, optical brighteners, polyester soil release agents, hydrotropes and gel-control agents, freeze-thaw stabilizers, bacteriocides, preservatives, suds control agents, bleach activators and the like. Fabric softeners, especially clays and mixtures of clays with various amines and quaternary ammonium compounds, can all be used in the compositions. Such matters are well-known from the patent literature and in commercial practice.

The compositions herein are prepared using conventional techniques, well-known to the formulator of commercial detergent and bleach products.

Fabric conditioning agents, when present in the laundry product compositions, typically comprise between about 1% and about 35% of the composition, preferably between about 6% and about 25%. The particular fabric conditioning agent utilized is not believed to be critical to the present invention, and any of those fabric conditioning agents known in the art are believed to be applicable. These include, for example, quaternary ammonium fabric conditioners, such as those disclosed in U.S. Patent 3,936,537, Baskerville et al., issued February 3, 1976, tertiary amines, such as those disclosed in British Patent 1,514,276, Kenyon,

published June 14, 1978, amine-anion ion-pair complexes including those disclosed in British Patents 1,077,103 and 1,077,104, assigned to Bayer, published July 26, 1977, and U.S. Serial No. 153,172, Caswell, filed February 8, 1988, and smectite-type clay softening systems, such as those described in U.S. Patent 4,062,647, Storn et al., issued December 13, 1977, British Patent 1,483,627, assigned to Procter & Gamble, published Aubust 24, 1977.

Aqueous dispersions useful for direct application to articles of clothing in an aerosol form comprise a thiol heterocyclic deodorant agent; from about 0.1% to 10% water; from about 0.01% to about 5% of a suitable organic solvent; the balance being a suitable propellant. Examples of such propellants are the chlorinated, fluorinated and chlorofluorinated lower molecular weight hydrocarbons. Nitrous oxide, carbon dioxide, isobutane and propane may also be used as propellant gases. These propellants are used at a level sufficient to expel the contents of the container. Suitable organic materials useful as the solvent or a part of a solvent system are as follows: propylene glycol, polyethylene glycol (M.W. 200-600), polypropylene glycol (M.W. 425-2025), glycerine, sorbitol esters, 1,2,6-hexanetriol, deithyl tartrate, butanediol, and mixtures thereof. The balance of the composition comprises a liquid carrier, preferably the carrier is water or a mixture of water and monohydric alcohols.

Liquid fabric-treatment compositions can be prepared by mixing the thiol heterocyclic deodorant agent into a solvent, alone or with other components.

The deodorant agents of the present invention can be added to granular carriers by admixing the deodorant agent in solution with other of the composition's ingredients prior to the time when they are spray dried, and then spray drying said mixture in a conventional manner. Alternatively, granular or powder laundry product compositions can be made by dry blending the deodorant agents with other of the composition ingredients.

C. Fabric Treatment Compositions

Another aspect of the present invention involves fabric treatment compositions comprising thiol heterocyclic agents of the present invention for deposition onto articles of clothing or fabric worn in the vicinity of the skin, and a fabric treatment carrier. A "fabric treatment carrier", as used herein, typically comprises one or more of the following components: optical brighteners, surfactants (preferably nonionic or ionic) or organic esters. The fabric treatment compositions can, it is believed, inhibit or reduce the formation of nonmicrobial malodor due to axilla or crotch area sweat that has been absorbed by said clothing. Fabric treatment carriers include liquid and granular fabric conditioning compositions, and stain and/or odor removing compositions formulated such that the thiol heterocyclic deodorant agent is deposited on articles of clothing prior to washing or drying of said articles, or prior to use or wearing of said articles, such that the deodorant agent is deposited upon an article and remains deposited at least during the initial period when the article is worn or used. Typically, such compositions will contain from about 0.01% to about 20% of the thiol heterocyclic compounds of the present invention, preferably from about 0.1% to about 10%.

D. Catamenials and Diapers

Another aspect of the present invention involves compositions to control nonmicrobial malodor comprising an absorbent substrate carrier on a catamenial or diaper and a deodorant agent of the present invention. "Absorbent substrate carrier", as used herein, means an absorbent layer or core of material comprising wood pulp fiber, cotton fibers, polyester fibers or other liquid or solid absorbent materials. Deodorant compositions containing the deodorant agent of the present invention for use to control urine-based and menstrual fluid-based malodor can include, but are not limited to, catamenial products such as sanitary napkins and panty liners and infant and adult diapers. Another aspect of the present invention provides deodorant and deodorant/anti-septic compositions comprising the deodorant agent of the present invention and perfumes or antimicrobial agents for use in urinals and toilets, catamenials, and bedding.

E. Methods

The present invention also provides methods for controlling or inhibition of malodor, preferably malodor of human perspiration comprising topically applying a safe and effective amount of one or more of the thiol heterocyclic compositions of the present invention to areas of the skin subject to secretion of both apocrine and eccrine sweat, i.e., the axilla and crotch areas of the body.

Methods of using the composition of the present invention to control nonmicrobial malodor comprise topically applying compositions of the present invention; the compositions are preferably applied such that from about 0.002 mg to about 4.0 mg, preferably from about 0.01 mg to about 1.0 mg, of the deodorant agent is applied per one square centimeter of skin.

Additionally, the present invention provides methods of controlling nonmicrobial malodor in articles of clothing and fabric by depositing a safe and effective amount of a thiol heterocyclic agent of the present invention to an area of the article of clothing of fabric. Preferably the deodorant composition is applied to the article of clothing at areas which typically come in contact with both eccrine gland and apocrine gland perspiration when worn, particularly the axilla and crotch regions. Preferably, from about 0.002 to about 4.0, preferably from about 0.01 to about 1.0, milligrams of the thiol heterocyclic deodorant agent is deposited per one square centimeter of the article of clothing or fabric.

The present invention also provide methods of contacting an article of clothing or fabric with an aqueous detergent solution comprising from about 0.1% to about 2% by weight of a detergent composition of the present invention. Fabrics to be laundered are agitated, preferably in an automatic washing machine, in these solutions to effect cleaning, stain removal, fabric care benefits, and malodor control. Compositions can also be applied to articles of clothing or fabric by tumbling said articles with the composition in an automatic laundry dryer.

The present invention also provides methods of controlling malodor comprising contacting or depositing a thiol heterocyclic deodorant agents of the present invention to catamenial products that come into contact with urine, feces and/or menstrual fluid. Preferred methods further comprising contacting or depositing the deodorant agents to catamenial products comprising an absorbent substrate carrier.

The following non-limiting examples illustrate compositions of the present invention.

EXAMPLES

Examples I - XXIV

Deodorant compositions of a gel-type solid form are made comprising the ingredients listed in Tables I - IV.

Table I

Ingredient	I	II	III	IV	V	VI
2,4-diamino-6-mercapto pyrimidine	0.5	-	-	-	-	-
2-thiouracil	-	0.5	-	-	-	-
4,5-diamino-6-hydroxy-2-mercaptopyrimidine	-	-	0.5	-	-	-
2-mercaptobenzoxazole	-	-	-	0.5	-	-
2-mercaptopyridine	-	-	-	-	0.5	-
2-thiohistidine	-	-	-	-	-	0.5
ethanol	5.0	5.0	5.0	5.0	5.0	5.0
EDTA [1]	1.0	1.0	1.0	1.0	1.0	1.0
water	93.5	93.5	93.5	93.5	93.5	93.5

[1]: ethylenediamine tetraacetic acid, chelating agent

Table II

Ingredient	VII	VIII	IX	X	XI	XII
2,4-diamino-6-mercapto pyrimidine	3.0	-	-	-	-	-
2-thiouracil	-	3.0	-	-	-	-
4,5-diamino-6-hydroxy 2-mercaptopyrimidine	-	-	3.0	-	-	-
2-mercaptobenzoxazole	-	-	-	3.0	-	-
2-mercaptopyridine	-	-	-	-	3.0	-
2-thiohistidine	-	-	-	-	-	3.0
ethanol	41.0	41.0	41.0	41.0	41.0	41.0
triclosan*	0.3	0.3	0.3	0.3	0.3	0.3
cetyl alcohol	5.0	5.0	5.0	5.0	5.0	5.0
propylene glycol	41.4	41.4	41.4	41.4	41.4	41.4
cyclomethicone (D5[2])	5.0	5.0	5.0	5.0	5.0	5.0
dibenzaldehyde monosorbitol acetal	3.0	3.0	3.0	3.0	3.0	3.0
colorants	1.3	1.3	1.3	1.3	1.3	1.3

[2]: cyclomethicone D5 supplied by Dow Corning Corp.
*: triclosan supplied by Aldrich Chemical Company

Table III

Ingredient	XIII	XIV	XV	XVI	XVII	XVIII
2,4-diamino-6-mercapto pyrimidine	1.0	-	-	-	-	-
2-thiouracil	-	1.0	-	-	-	-
4,5-diamino-6-hydroxy 2-mercaptopyrimidine	-	-	1.0	-	-	-
2-mercaptobenzoxazole	-	-	-	1.0	-	-
2-mercaptopyridine	-	-	-	-	1.0	-
2-thiohistidine	-	-	-	-	-	1.0
cyclomethicone (D5)	44.0	44.0	44.0	44.0	44.0	44.0
macrospherical ZAG complex [3]	26.7	26.7	26.7	26.7	26.7	26.7
stearyl alcohol	11.0	11.0	11.0	11.0	11.0	11.0
Fluid AP [4]	5.0	5.0	5.0	5.0	5.0	5.0
talc	6.5	6.5	6.5	6.5	6.5	6.5
fragrance	0.8	0.8	0.8	0.8	0.8	0.8

[3]: zirconium-aluminum-glycine hydroxy chloride complex antiperspirant material

[4]: water insoluble ether, condensation product of about 14 moles propylene oxide with one mole butyl alcohol, sold by Union Carbide Corporation

Table IV

Ingredient	XIX	XX	XXI	XXII	XXIII	XXIV
2,4-diamino-6-mercapto pyrimidine	3.0	-	-	-	-	-
2-thiouracil	-	3.0	-	-	-	-
4,5-diamino-6-hydroxy 2-mercaptopyrimidine	-	-	3.0	-	-	-
2-mercaptobenzoxazole	-	-	-	3.0	-	-
2-mercaptopyridine	-	-	-	-	3.0	-
2-thiohistidine	-	-	-	-	-	3.0
ethanol	46.8	46.8	46.8	46.8	46.8	46.8
propylene glycol	46.9	46.9	46.9	46.9	46.9	46.9
dibenzaldehyde monosorbitol acetate	3.3	3.3	3.3	3.3	3.3	3.3

The compositions, comprised as above, are made by admixing the components. The mixture is heated to approximately 88°C and stirred. The mixture is then poured into stick-forms and solidified rapidly upon cooling.

Examples XXV - XXXVI

Deodorant compositions of a gel-type solid are made comprising the ingredients listed in Tables V and VI.

Table V

Ingredient	XXV	XXVI	XXVII	XXVIII	XXIX	XXX
2,4 diamino-6-mercapto pyrimidine	.01	.1	1.0	5.0	10.0	20.0
dipropylene glycol	28.4	28.4	28.4	28.4	28.4	28.4
myristyl ether	21.0	21.0	21.0	21.0	21.0	21.0
cyclomethicone (D5)	19.8	19.7	18.8	14.8	9.8	4.8
sodium stearate	6.0	6.0	6.0	6.0	6.0	6.0
stearic acid	0.5	0.5	0.5	0.5	0.5	0.5
ethanol	24.0	24.0	24.0	24.0	24.0	24.0
triclosan	0.3	0.3	0.3	0.3	0.3	0.3

Table VI

Ingredient	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI
2,4 diamino-6-mercapto pyrimidine	.01	.1	1.0	5.0	10.0	20.0
dipropylene glycol	28.4	28.4	28.4	28.4	28.4	28.4
myristyl ether	21.0	21.0	21.0	21.0	21.0	21.0
cyclomethicone (D5)	19.8	19.7	18.8	14.8	9.8	4.8
sodium stearate	6.0	6.0	6.0	6.0	6.0	6.0
stearic acid	0.5	0.5	0.5	0.5	0.5	0.5
ethanol	24.0	24.0	24.0	24.0	24.0	24.0

The compositions, comprised as above, are made by admixing the components. The mixture is heated to approximately 88°C and stirred. The mixture is then poured into stick-forms and solidified rapidly upon cooling.

EXAMPLE XXXVII

A liquid deodorant comprised as below is prepared.

Component	% (by weight)
2-thiohistidine	1.0
triclosan	0.5
water	92.5
ethanol	5.0
EDTA	1.0

The above components are admixed and placed in a conventional pump-spray apparatus. The composition can be sprayed directly onto axilla and crotch areas of the skin, or onto axilla and crotch areas of articles of clothing.

EXAMPLE XXXVIII

A deodorant composition in aerosol form, according to the present invention, is made comprising:

Component	% (by weight)
2-thiohistidine	1.0
triclosan	0.4
ethanol	14.8
propylene glycol	14.8
isobutane (propellant)	70.0

An aerosol deodorant, comprised as above, is made by admixing the 2-thiohistidine, triclosan, ethanol, and propylene glycol and placing the mixture in a conventional aerosol can. The propellant is then added, under pressure, and the can sealed.

EXAMPLE XXXVIX

A liquid deodorant composition for topical application to the skin with a pump spray bottle is made comprising:

Component	% (by weight)
glycerol	49.8
ethanol	49.8
triclosan	0.3
4,5 diamino-6-hydroxy-2-mercaptopyrimidine	0.1

The liquid deodorant is prepared by admixing the components noted above, adjusting the mixture to pH 9.0 with NaOH, and placing the mixture in a conventional pump spray bottle.

EXAMPLE XXXX

A liquid deodorant composition for topical application to the skin with a roll-on bottle is made comprising:

Component	% (by weight)
glycerol	49.8
ethanol	49.8
triclosan	0.3
2-thiohistidine	0.1

The liquid deodorant is prepared by admixing the components noted above, adjusting the mixture to pH 9.0 with NaOH, and placing the mixture in a conventional roll-on bottle.

EXAMPLE XXXXI

The purpose of this example is to exemplify the effectiveness of the present invention for neutralizing and inhibiting non-microbial malodor.

A variety of thiol heterocyclic deodorant agents were added to the concentrated artificial sweat in in vitro tests. Sterile concentrated artificial sweat was prepared containing an aqueous pyridoxal phosphate solution and an aqueous solution containing natural apocrine gland secretion. The concentrated artificial sweat for each of the tests was prepared according to the following procedure, though not necessarily at the same time for each of the tested deodorant agents. The aqueous pyridoxal phosphate solution contained 12.4 mg pyridoxal phosphate per 10 ml of 20 mM tris(hydroxymethyl) amino methane, adjusted to pH 7.5 with HCl.

Natural human apocrine gland secretions were collected by firmly rolling the ball of a conventional deodorant roll-on bottle against the skin in the axilla region for at least six known malodor substrate producers for one minute each. The roll-on bottles, prior to collection of apocrine secretions, each contained 10 ml of 20 mM of tris(hydroxymethyl) amino methane adjusted to pH 7.5 with HCl. The apocrine gland secretion solutions from each bottle were then mixed together and sterilized by filtration through a 0.22 micron acetate membrane and then heat treated for 30 minutes at 80 °C. The apocrine gland secretion was sterilized to eliminate the occurrence of microbial malodor during the test.

The artificial sweat composition was prepared by mixing one volumetric part of the pyridoxal phosphate solution with five volumetric parts of the solution containing apocrine gland secretion, under sterile conditions.

The thiol heterocyclic deodorant agents were added to 6.0 ml samples of artificial sweat composition at 0.7 mM concentration under sterile conditions and incubated for 48 hours at 37 °C.

At the end of the incubation period, the sweat samples were organoleptically evaluated by sniffing the contents and comparing the smell to a control sample of said sweat which was incubated during the same period and under the same conditions as the deodorant agent-containing samples, but did not contain any thiol heterocyclic deodorant agent. A strong malodor was observed at the end of the incubation period for the control samples.

The following thiol heterocyclic compounds were tested at 0.7 mM concentrations in the artificial sweat (corresponding approximate gram amounts added are indicated in parenthesis): 2,4-diamino-6-mercapto pyridine (0.7 mg); 2-thiouracil (.6 mg); 4,5-diamino-6-hydroxy-2-mercaptopyrimidine (0.8 mg); 2-mercaptobenzoxazole (.8mg); 2-mercaptopyridine (0.6 mg); and L-thiohistidine (0.9 mg). In each case, the thiol heterocyclic compound substantially reduced the occurrence of nonmicrobial malodor relative to the corresponding control sample.

It was also observed that malodor from a sweat sample prepared substantially the same way as the control samples above was significantly reduced, i.e., neutralized, by the addition of 4,5-diamino-6-hydroxy-2-mercapto pyridine at 0.7 mM concentrations in the sweat sample subsequent to incubation.

EXAMPLE XXXXII

A granular detergent composition for household laundry use is as follows:

Component	Amount(%)
Sodium C_{14}-C_{15} alkylsulfate	13.3
Sodium C_{13} linear alkyl benzene sulfonate	5.7
C_{12}-C_{13} alkylpolyethoxylate (6.5)	1.0
Sodium toluene sulfonate	1.0
*TMS/TDS, sodium salt, 86/14 weight ratio of TMS:TDS	25.0
Sodium N-hydroxyethylethylenediaminetriacetate	2.0
Sodium polyacrylate (Avg. M.W. approx. 5000)	2.0
Sodium carbonate	20.3
Sodium silicate	5.8
Polyethylene glycol (Avg. M.W. approx. 8000)	1.0
2-thiohistidine	1.0
Sodium sulfate, water and miscellaneous**	29.1
	100.0

*TMS/TDS - mixture of tartrate monosuccinate and tartrate disuccinate in a TMS to TDS weight ratio of 85/15 sodium salt free

**includes perfume, buffers, colorants, opacifiers and the like

The components are added together with continuous mixing with sufficient extra water (about 40% total) to form an aqueous slurry which is then spray dried to form the composition. Ergothioneine or other thiol heterocyclic compounds useful in the composition of the present invention may be substituted for the above thiol heterocyclic compounds in the composition.

EXAMPLE XXXIII

A liquid detergent composition for household laundry use is as follows:

Component	Amount(%)
Potassium C_{14}-C_{15} alkyl polyethoxy (2.5) sulfate	8.3
C_{12}-C_{14} alkyl dimethyl amine oxide	3.3
Potassium toluene sulfonate	5.0
Monoethanolamine	2.3
TMS/TDS triethanolamine salt, 85/15 TMS/TDS	15.0
Potassium salt of 1,2-dihydroxy-3,5-disulfobenzene	1.5
Potassium polyacrylate (avg. M.W. approx. 9000)	1.5
2-thiohistidine	1.0
Water and miscellaneous*	62.1
	100.0

*includes perfume, buffers, colorants, opacifiers and the like

The components are added together with continuous mixing to form the composition. Ergothioneine or other thiol heterocyclic compounds useful in the composition of the present invention may be substituted for the above thiol heterocyclic compounds in the composition.

EXAMPLE XXXXIV

Fabric Conditioning Agent

Component	Amount(%)
Ditallow di-methyl ammonium chloride (DTDMAC)	3.7
Methyl-1-tallow amido ethyl 2-tallow imidazoline	3.7
2,2'-Dipyridaldisulfide	3.0
Water and miscellaneous*	89.6
	100.0

*includes perfume, buffers, colorants, opacifiers and the like

EXAMPLE XXXXV

Additional granular detergent compositions of the present invention comprise the following ingredients:

Ingredient	Percent (wt)
Sodium 12.3 linear alkyl benzene sulfonate	15.8
Sodium C_{14}-C_{15} alkyl sulfate	6.8
C_{12}-C_{13} alcohol ethoxylate (EO 6)	0.5
Sodium tripolyphosphate	6.8
Sodium pyrophosphate	13.1
Sodium acid pyrophosphate	12.4
Sodium silicate (1.6 ratio NaO/SiO_2)	7.6
Polyethylene glycol 8000	0.6
Sodium polyacrylate (MW 4500)	3.4
Protease enzyme*	1.8
Sodium perborate tetrahydrate	1.9
Sodium sulfate	14.4
4,5-Diamino-6-hydroxy-2-mercaptopyrimidine	.05
Balance (including water, brightener, perfume, suds suppressor)	14.85
	100.0
pH 1% aqueous solution at 20°C	9.2

*Reported in Anson units per gram

Aqueous crutcher mixes of the detergent compositions are prepared and spray-dried, except for the, sodium acid pyrophosphate, enzyme, and perfume, which are admixed, so that they contain the above ingredients at the levels shown.

EXAMPLE XXXXVI

An additional granular detergent composition for household laundry use is as follows:

Component	Amount(%)
Sodium C_{14}-C_{15} alkylsulfate	13.3
Sodium C_{13} linear alkyl benzene sulfonate	5.7
C_{12}-C_{13} alkylpolyethoxylate (6.5)	1.0
Sodium toluene sulfonate	1.0
*TMS/TDS, sodium salt, 86/14 weight ratio of TMS:TDS	25.0
Sodium N-hydroxyethylethylenediaminetriacetate	2.0
Sodium polyacrylate (Avg. M.W. approx. 5000)	2.0
Sodium carbonate	20.3
Sodium silicate	5.8
Polyethylene glycol (Avg. M.W. approx. 8000)	1.0
2,4-Diamino-6-mercaptopyrimidine	0.05
Sodium sulfate, water and miscellaneous**	22.85
	100.0

*TMS/TDS - mixture of tartrate monosuccinate and tartrate disuccinate in a TMS to TDS weight ratio of 85/15 sodium salt form

**includes perfume, buffers, colorants, opacifiers and the like

The components are added together with continuous mixing with sufficient extra water (about 40% total) to form an aqueous slurry which is then spray dried to form the composition.

EXAMPLE XXXXVII

An additional liquid detergent composition for household laundry use is as follows:

Component	Amount(%)
Potassium C_{14}-C_{15} alkyl polyethoxy (2.5) sulfate	8.3
C_{12}-C_{14} alkyl dimethyl amine oxide	3.3
Potassium toluene sulfonate	5.0
Monoethanolamine	2.3
TMS/TDS triethanolamine salt, 85/15 TMS/TDS	15.0
Potassium salt of 1,2-dihydroxy-3,5-disulfobenzene	1.5
Potassium polyacrylate (avg. M.W. approx. 9000)	1.5
2-Thiohistidine	0.01
Water and miscellaneous*	63.09
	100.0

*includes perfume, buffers, colorants, opacifiers and the like

The components are added together with continuous mixing to form the composition.

EXAMPLE XXXXVIII

Fabric Conditioning Agent

Component	Amount(%)
Ditallow di-methyl ammonium chloride (DTDMAC)	3.7
Methyl-1-tallow amido ethyl 2-tallow imidazoline	3.7
2-Mercaptopyrydine	0.1
Water and miscellaneous	92.5
	100.0

The disclosed thiol heterocyclic compounds control a variety of other malodors in addition to human perspiration. Such other malodors include, but are not limited to, environmental odors and chemical odors. In addition, the disclosed thiol heterocyclic compounds control negative odors generated by or deposited on various porous and nonporous surfaces including, but not limited to, plastics, wood, hair, glass, porcelain, fabric, fibers of varying compositions, foods, and beverages. Such negative odors may be controlled by applying the thiol heterocyclic compound to said surfaces before, during or after the odor has been generated, or by incorporating the thiol heterocyclic compound into these surfaces during manufacture. As used herein, "control odors, malodors, or negative odors" means preventing, retarding, or reversing such odor formation. As used herein, "negative odor or malodor" means an odor emanating from a particular surface or manufacture which is undesirable.

Applicants have further determined that the disclosed thiol heterocyclic compounds, preferably 4,5-diamino-6-hydroxy-2-mercaptopyrimidine, 2,4-diamino-6-mercaptopyrimidine, 2-thiohistidine, 2-mercaptopyridine, and 4-mercaptopyridine, are highly effective in controlling malodors associated with a laundry cleaning product. Though the mechanism upon which this deodorization is based is unknown, it is believed to be something beyond an interaction with vitamin B_6 reactions. Such a surprising application is extremely useful in laundry product compositions which do not comprise a perfume, as these compositions often have negative odors emanating from their substituents including, but not limited to, solvents, enzymes, surfactants, or contaminants. In addition to deodorizing these negative odors, the thiol heterocyclic deodorant agent enhances positive odors in the laundry product, such as perfumes.

The present invention further relates to compositions effective for controlling malodors associated with chemical formulations of laundry cleaning products. Laundry product compositions with reduced negative laundry product odor comprise from about .001% to about 20% of a thiol heterocyclic compound.

The present invention further relates to methods effective for controlling malodors associated with chemical formulations of laundry cleaning products. Methods for controlling negative laundry product odors comprise inclusion of from about .001% to about 20% of a thiol heterocyclic compound in a laundry product composition.

Claims

1. A deodorant composition for controlling malodor from perspiration characterized in that it comprises:
   a) a safe and effective amount of a thiol heterocyclic compound
      (i) wherein said compound has a heterocyclic ring structure having at least one heteroatom, preferably from 1 to 3 heteroatoms, in the ring structure selected from oxygen, nitrogen, and sulfur, preferably nitrogen, wherein preferably the nitrogen heteroatom(s) is(are) not bonded directly to an oxygen atom to form a N-oxide;
      (ii) wherein the heterocyclic ring structure has at least 1 thiol substituent attached to a carbon atom of said heterocyclic ring; and
      (iii) wherein preferably the ring structure is unsubstituted, other than thiol substituent(s), or substituted on carbon atoms of the ring structure, wherein said substituents (other than thiol) are selected from hydroxy, amino, and substituted or unsubstituted alkyl; and
   b) a topical carrier;
   whereby the composition is suitable for application to the skin or to articles of clothing worn in the vicinity of the skin.

2. A deodorant composition for controlling malodor from perspiration, according to Claim 1 characterized in that it further comprises an antimicrobial deodorant agent.

3. A deodorant composition for controlling malodor from perspiration, according to Claim 1 or 2, characterized in that the thiol heterocyclic compound is selected from heterocyclic compounds having a thiol substituted heterocyclic ring with a delocalized electron structure, where at least one thiol substituent is
   a) attached to a heterocyclic ring carbon atom that is double bonded to a heterocyclic ring nitrogen or sulfur atom,
   b) attached to a carbon atom of said heterocyclic ring that is connected to a nitrogen or sulfur atom of said heterocyclic ring by conjugated double bonds, or
   c) attached to a heterocyclic ring carbon atom which is bonded to a heterocyclic ring oxygen atom or which is double bonded to a heterocyclic ring carbon atom that is adjacent to a heterocyclic ring oxygen atom.

4. A deodorant composition for controlling malodor from perspiration, according to Claim 3, characterized in that the thiol heterocyclic compound is selected from thiol derivatives of thiophene, furan, pyran, isobenzofuran, chromene, pyrrole, imidazole, pyrazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, isoindole, indole, purine, quinolizine, isoquinoline, quinoline, phthalazine, naphthyridine, quinoxaline, quinozoline, cinnoline, pteridine, oxazoline, isothiazole, oxazole, and isoxazole, preferably pyridine, pyrimidine, quinoline, and imidazole.

5. A deodorant composition for controlling malodor from perspiration, according to Claim 4, characterized in that the thiol heterocyclic compound is selected from 5,6 diamino-2-thiouracil, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine, 2-thiouracil, 2,4-diamino-6-mercaptopyrimidine hemisulfate, ergothioneine, 2-thiohistidine, 2-mercaptopyridine, 4-mercaptopyridine, 2,mercaptobenzoxazole, 2-mercapto-6-nitrobenzothiazole, 2-thiocytosine, 6-thioxanthine, 2,6-dimercaptopyridine, 2-mercapto-5-nitropyridine, 2-mercaptoquinoline, 2-mercapto-4-hydroxy-6,8-dichloroquinazoline, 2-mercaptopyrimidine, 4-mercaptoquinazoline, 2-phenyl-4-quinazolinethiol, 3-amino-6-methyl-4-pyridazinethiol, 5-amino-4-pyridazinethiol, alpha-tocopherthiol, 2-amino-6,7-dimethyl-4-pteridinethiol, 4-mercaptopteridine, 2-mercapto-4-hydroxypteridine, and 2,4-diamino-6-phenyl-7-pteridinethiol, preferably 2-mercaptopyridine, 4-mercaptopyridine, 2,4-diamino-6-mercaptopyrimidine, 2-thiohistidine, and ergothioneine.

6. A method for controlling malodor from perspiration characterized in that it comprises topically applying to skin in the axilla or crotch region, a safe and effective amount of the composition of any of Claims 1-5.

7. A deodorant composition characterized in that it comprises:
a) a safe and effective amount of a thiol heterocyclic compound wherein said compound has a heterocyclic ring structure having at least one heteroatom in the ring structure selected from oxygen, nitrogen, and sulfur; and wherein the heterocyclic ring structure has at least 1 thiol substituent attached to a carbon atom of the heterocyclic ring; and
b) a laundry product carrier.

8. A deodorant composition, according to Claim 7, characterized in that the thiol heterocyclic compound is selected from thiol derivatives of pyridine, pyrimidine, quinoline and imidazole.

9. A deodorant composition characterized in that it comprises:
a) a safe and effective amount of a thiol heterocyclic compound wherein said compound has a heterocyclic ring structure having at least one heteroatom in the ring structure selected from oxygen, nitrogen, and sulfur; and wherein said heterocyclic ring structure has at least 1 thiol substituent attached to a carbon atom of said heterocyclic ring; and
b) a fabric treatment carrier.

10. A method for controlling malodor from articles of clothing characterized in that it comprises deposition of a safe and effective amount of the composition of any of Claims 8 or 9 to an article of clothing.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 1982

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	DE-A-2 410 610 (ORREN) * Claims 1,6; page 9, lines 24-27 * ---	1-10	A 61 K 7/32 A 61 L 9/01
X	EP-A-0 023 676 (REWO) * Claims 1,2,4; example 4 * ---	1-4	
A	PATENT ABSTRACTS OF JAPAN, vol. 10, no. 355 (C-388)[2411], 29th November 1986; & JP-A-61 155 302 (SANSHO SEIYAKU K.K.) 15-07-1986 * Abstract * ---	1-5	
A	CHEMICAL ABSTRACTS, vol. 102, no. 24, June 1985, page 338, abstract no. 209142s, Columbus, Ohio, US; & JP-A-60 16 907 (POLA CHEMICAL INDUSTRIES) 28-01-1985 * Abstract * ---	1-5	
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TECHNICAL FIELDS SEARCHED (Int. Cl.5)

A 61 K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-08-1991	WILLEKENS G.E.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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(54) **Liquid antiperspirant composition**

Flüssige schweisshemmende Zusammensetzung

Composition antiperspirante liquide

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(73) Proprietor: **THE PROCTER & GAMBLE COMPANY**
Cincinnati, Ohio 45202 (US)

(72) Inventors:
- **Orr, Thomas Vincent**
  Cincinnati, Ohio 45239 (US)
- **Newcomer, Patricia Jane**
  Cincinnati, Ohio 45241 (US)

(74) Representative: **Brooks, Maxim Courtney et al**
Newcastle-upon-Tyne NE12 9TS (GB)

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Description

The present invention relates to liquid antiperspirant compositions containing silicone fluid with reduced incidence of in-use skin irritation. More particularly, this invention relates to liquid antiperspirant compositions containing silicone fluid especially useful for roll-on antiperspirant application with reduced incidence of in-use skin irritation, in combination with excellent cosmetic properties.

Antiperspirant compositions have become a part of many persons' personal care and grooming regimen. The antiperspirant active materials which have been typically used include astringent metallic (e.g., aluminum, zinc, and zirconium) salts such as salts of aluminum halides, aluminum hydroxyhalides, zirconyl oxyhalides, zirconyl hydroxyhalides, and complexes of aluminum, zirconium and amino acid (e.g., glycines). These materials, naturally, are sensitive to the presence of water and are preferably stored and delivered to the skin in the substantial absence of water in order to preserve efficacy. Additionally, it is generally perceived as unpleasant for the antiperspirant composition to have a "wet" feel upon application to the skin. Hence, it is also desirable to deliver the antiperspirant active to the skin by a vehicle which minimizes this feeling of wetness. The delivery vehicle must also not cause excessive staining of the user's clothing, and should control or reduce chalky appearance on the skin (and potential rub-off onto the user's clothes) resulting from the antiperspirant active, suspension agent, or other material in the composition. For these reasons, a variety of volatile silicones and non-volatile silicone emollients, and combinations thereof, have commonly been utilized in liquid antiperspirant compositions for delivery of the antiperspirant active material.

The primary silicone material used in recent times for delivery of antiperspirant actives in roll-on liquid antiperspirant applications is volatile cyclomethicone. Volatile cyclomethicone provides a very dry feel upon application and has a low heat of evaporation. The low viscosity of the volatile fluids is also important for providing an easily flowable composition for roll-on or aerosol application. In many of these compositions, a relatively low level of certain non-volatile silicone fluids, or other non-volatile emollient such as paraffin oil (e.g., mineral oil) is also included. These non-volatile fluids generally have a high enough viscosity so that they remain deposited on the skin throughout a significant portion of the day. They also inhibit occurrence of, and consequently rub-off of, chalk-like residue formed from the antiperspirant composition's particulate ingredients. These non-volatile materials are typically utilized at relatively low levels (1% to 12%) to minimize an undesirable "greasy feel which they can impart.

Liquid roll-on antiperspirant compositions such as these are exemplified in numerous publications including US-A-4,863,721, Beck et al., issued September 5, 1989. EP-A-330,140, published August 30, 1989, and US-A-4,423,041, Clum et al., issued December 27, 1983.

Other liquid emollients have also been used in liquid antiperspirant compositions. These include paraffins such as mineral oil, and a variety of alcohols and esters of alcohols and fatty acids. However, these emollients also have drawbacks which, typically, include skin irritation and greasy feel.

Whereas liquid antiperspirant compositions containing high levels of volatile silicone have provided consumer-acceptable performance and have generally attained a following in the marketplace, the use of such antiperspirant compositions can produce skin irritation in the form of itching, redness, rash, and/or burning (alternately referred to as "stinging"), particularly when applied immediately or soon after shaving. Although the incidence of this is not experienced for all application usages or by all people, it would nevertheless be desirable to provide a liquid antiperspirant composition that could be used for roll-on applications which provide reduced incidence of skin irritation while still providing excellent cosmetic properties, e.g., low "wetness", low levels of "chalky" residue, and low levels of rub-off onto clothing. It would also be desirable to provide liquid antiperspirant compositions useful for aerosol application that have reduced incidence of in-use skin irritation and which retain excellent cosmetic properties. It is an object of this invention to provide such liquid antiperspirant compositions useful for both roll-on and aerosol applications.

It has been found that by formulation of liquid antiperspirant compositions with high levels of certain non-volatile polysiloxane fluids and low or zero levels of conventional volatile polysiloxane fluids, reduced levels of skin irritation can be attained while maintaining excellent overall cosmetic properties.

Thus, the present invention relates to reduced skin irritation liquid antiperspirant compositions that can be used for roll-on antiperspirant application which comprise an antiperspirant active material and, as the major silicone fluid ingredient, non-volatile polysiloxane fluid having an average viscosity of 10 mm^2s^{-1} to 50 mm^2s^{-1} at 25°C. Volatile silicone fluids, such as the cyclic polysiloxanes (e.g., cyclomethicone), can be present, but in keeping with the invention, the level thereof should not exceed 15%, by weight, of the composition. A suspension agent will also be present in the compositions thereof in an amount sufficient to improve suspendability of the antiperspirant active and thereby enhance consistent, even antiperspirant active delivery to the skin.

In a preferred embodiment for roll-on application, the present invention will encompass liquid antiperspirant compositions comprising:

(a) from 10% to 70%, by weight, of a particulate antiperspirant active material;
(b) from 1% to 15%, by weight, of a suspension agent component;
(c) from 0% to less than 5%, by weight of a volatile silicone; and

(d) from 25% to 75%, by weight, of a non-volatile silicone fluid component having an average viscosity of from 10 mm^2s^{-1} (centistokes) to 50 mm^2s^{-1} (centistokes) at 25°C.

In a preferred embodiment for aerosol application, the present invention will encompass compositions comprising from 5% to 80% of a liquid antiperspirant concentrate composition, as described immediately above in (a), (b), (c), and (d), and from 20% to 95% of an aerosol propellant.

The essential as well as various optional components that can be used in the compositions of the present invention are described below. All percentages given herein are weight percentages of the composition, unless otherwise specifically indicated.

An essential component of the present compositions is an antiperspirant active material. Any particulate compound or composition or mixture thereof having antiperspirant activity can be used. Astringent metallic salts are preferred antiperspirant materials for use herein, particualy including inorganic and organic salts of aluminum, zirconium, and zinc, and mixtures thereof. Particularly preferred are the aluminum and zirconium salts such as aluminum halides, aluminum hydroxy halides, zirconyl oxide halides, and zirconyl hydroxy halides, and complexes of aluminum, zirconium, and/or zinc with amino acids, e.g., glycines.

Specific, exemplary aluminum salts that can be used include aluminum chloride and the aluminum hydroxyhalides having the general formula $Al_2(OH)_aQ_b.XH_2O$ where Q is chloride, bromide, or iodide (preferably chloride); a is from 2 to 5, and a + b = 6 , and a and b do not need to be integers; and where X is from 1 to 6, and X does not need to be an integer. Particularly preferred are the aluminum chlorhydroxides referred to as "5/6 basic chlorhydroxide" wherein a is 5 and "2/3 basic chlorhydroxide" wherein a is 4. Aluminum salts of this type can be prepared in the manner described more fully in US-A-3,887,692, Gilman, issued June 3, 1975; US-A-3,904,741, Jones and Rubino, issued September 9, 1975; US-A-4,359,456, Gosling et al., issued November 16, 1982; and GB-A-2,048,229, Fitzgerald et al., published December 10, 1980. Mixtures of aluminum salts are described in GB-A-1,347,950, Shin, et al., published February 27, 1974.

The zirconium compounds which may be used in the present invention include both zirconium oxy salts and zirconium hydroxy salts, also referred to as the zirconyl salts and zirconyl hydroxy salts. These are preferred compounds for use herein and may be represented by the following general empirical formula:

$$ZrO(OH)_{2-nz}B_z$$

wherein z may vary from 0.9 to 2 and need not be an integer; n is the valence of B; 2-nz is greater than or equal to 0; and B may be selected from the group consisting of halides (preferably chloride), nitrate, sulfamate, sulfate, and mixtures thereof. Although only zirconium compounds are exemplified in this specification, it will be understood that other Group IVB metal compounds, including hafnium, could be used in the present invention.

As with the basic aluminum compounds discussed above, it will be understood that the above formula is intended to represent and include compounds having coordinated and/or bound water in various quantities, as well as polymers, mixtures and complexes of the above. As will be seen from the above formula, the zirconium hydroxy salts actually represent a range of compounds having various amounts of the hydroxy group, varying from about 2.0 to only slightly greater than 0 groups per molecule.

Several types of antiperspirant complexes utilizing the above antiperspirant salts are known in the art. For example, US-A-4,120,948, Shelton, issued October 17, 1978 and US-A-3,792,068, Luedders et al., issued February 12, 1974, disclose complexes of aluminum, zirconium, and amino acids such as glycines. These complexes and other similar compleses with glycine amino acids are commonly known as ZAG complexes. ZAG complexes useful herein are identified by the specification of both the molar ratio of aluminum to zirconium (hereinafter "Al:Zr" ratio) and the molar ratio of total metal to chlorine (hereinafter "Metal:Cl" ratio). ZAG complexes useful herein have an Al:Zr ratio of from 1.67 to 12.5 and a Metal:Cl ratio of from 0.73 to 1.93.

Also useful are the ZAG complexes disclosed in GB-A-2,144,992, Callaghan et al., published March 20, 1985. These ZAG actives, when analyzed by high pressure gel permeation chromatography, exhibit a distribution pattern having four or more successive peaks or "bands" where the height ratio of Banks IV to III is greater than 2:1.

More preferred are ZAG actives which have a total area under the curve of bands I and II of less than 10%, preferably less than 5%, more preferably less than 2% and most preferably less than 1%.

Preferred ZAG complexes can be formed by

(A) co-dissolving in water

(1) one part $Al_2(OH)_{6-m}Q_m$, wherein Q is an anion selected from the group consisting of chloride, bromide,, and iodide; and m is from 0.8 to 2.0;

(2) x parts $ZrO(OH)_{2-a}Q_a.nH_2O$, where Q is chloride, bromide, or iodide; a is from 1 to 2; n is from 1 to 8; and x is from 0.16 to 1.2;

(3) p parts neutral amino acid selected from the group consisting of glycine, dl-tryptophane, dl-β-phenylalanine, dl-valine, dl-methionine, and β-alanine, and where p is from 0.06 to 0.53;

(B) co-drying the resultant mixture to a friable solid; and

(C) reducing the resultant dried inorganic-organic antiperspirant complex to a particulate form.

A preferred aluminum compound for preparation of such ZAG type complexes is aluminum chlorhydroxide of the empirical formula $Al_2(OH)_5Cl{\cdot}2H_2O$. Preferred zirconium compounds for preparation of such ZAG-type complexes are zirconyl hydroxychloride having the empirical formula $ZrO(OH)Cl{\cdot}3H_2O$ and the zirconyl hydroxyhalides of the empirical formula $ZrO(OH)_{2-a}Cl_2{\cdot}nH_2O$ wherein a is from 1.5 to 1.87, and n is from 1 to 7. The preferred amino acid for preparing such ZAG-type complexes is glycine of the formula $CH_2(NH_2)COOH$. Salts of such amino acids can also be employed in the antiperspirant complexes. See US-A-4,017,599, Rubino, issued April 12, 1977.

A wide variety of other types of antiperspirant complexes are also known in the art. For example, US-A-3,903,258, Siegal, issued September 2, 1975, discloses a zirconium aluminum complex prepared by reacting zirconyl chloride with aluminum hydroxide and aluminum chlorhydroxide. US-A-3,979,510, Rubino, issued September 7, 1976, discloses an antiperspirant complex formed from certain aluminum compounds, certain zirconium compounds, and certain complex aluminum buffers. US-A-3,981,896, issued September 21, 1976, discloses an antiperspirant complex prepared from an aluminum polyol compound a zirconium compound and an organic buffer. US-A-3,970,748, Mecca, issued July 20, 1976, discloses an aluminum chlorhydroxy glycinate complex of the appropriate general formula $[Al_2(OH)_4Cl][H_2CNH_2{\cdot}COOH]$.

Of all of the above types of antiperspirant actives, preferred compounds include the 5/6 basic aluminum salts of the empirical formula $Al_2(OH)_5Cl{\cdot}2H_2O$; mixtures of $AlCl_3{\cdot}6H_2O$ and $Al_2(OH)_5Cl{\cdot}2H_2O$ with aluminum chloride to aluminum hydroxychloride weight ratios of up to 0.5; ZAG type complexes wherein the zirconium salt is $ZrO(OH)Cl{\cdot}3H_2O$, the aluminum salt is $Al_2(OH)_5Cl.\ 2H_2O$ or the aforementioned mixtures of $AlCl_3{\cdot}6H_2O$ and $Al_2(OH)_5Cl.\ 2H_2O$ wherein the total metal to chloride molar ratio in the complex is less than 1.25 and the Al:Zr molar ratio is 3.3, and the amino acid is glycine; and the ZAG-type complexes wherein the zirconium salt is $ZrO(OH)_{2-a}Cl_a{\cdot}nH_2O$ wherein a is from 1.5 to 1.87 and n is from 1 to 7, the aluminum salt is $Al_2(OH)_5Cl{\cdot}2H_2O$, and the amino acid is glycine.

The most preferred antiperspirant actives useful in the compositions of the present invention are antiperspirant actives with enhanced efficacy due to improved molecular distribution. Aluminum chlorhydroxide salts, zirconyl hydroxychloride salts, and mixtures thereof having improved molecular distributions are known, having been disclosed, for example, in the following documents: US-A-4,359,456, Gosling et al., issued November 16, 1982; EP-A-183,171, Armour Pharmaceutical. Company, published June 4, 1986; GB-A-2,048,229, The Gillette Company, published December 10, 1980; EP-A-191,628, Unilever PLC, published August 20, 1986; and GB-A-2,144,992, The Gillette Company, published March 20, 1985.

The improved molecular distribution is determined by the known analysis method called gel permeation chromatography. This analysis method is described, for example, in several of the above patent specifications as well as in EP-A-7,191, Unilever Ltd., published January 23, 1980. It is preferred for purposes of the present invention that the antiperspirant actives utilized have enhanced efficacy due to improved molecular distribution with a ratio of peak 4 to peak 3 greater than 0.1:1 as determined by gel permeation chromatography. This ratio, as is recognized by one skilled in the art, relates to the relative area under those two peaks as measured by the gel permeation chromatography analysis method.

Highly desirable antiperspirant salts for use herein include aluminum chlorohydrex (sold under the name Rehydrol® (RTM), by Reheis Chemical Company), aluminum chlorohydrex PEG, aluminum chlorohydrex PG, aluminum sesquichlorohydrate, aluminum sesquichlorohydrex PEG, aluminum sesquichlorohydrex PG, and mixtures thereof, particularly aluminum sesquichlorohydrate.

The antiperspirant active material is present in the liquid antiperspirant compositions of the present invention at a level of from 10% to 70%, preferably from 15% to 60% These weight percentages are calculated on an anhydrous metal salt basis (exclusive of glycine, the salts of glycine, or other complexing agents).

Another essential component of the present invention is a non-volatile silicone fluid component. In addition to serving as a vehicle for antiperspirant active delivery to the skin, this component can act as an emollient, can inhibit formation of chalk-like residue common in many conventional liquid antiperspirant compositions, and can inhibit rub-off of the antiperspirant active material In use. The non-volatile fluid component can comprise one or more silicone fluid materials, but should have an "average" viscosity within the range of from 10 mm^2s^{-1} (centistokes) to 50 mm^2s^{-1} (centistokes), preferably from 15 mm^2s^{-1} (centistokes) to 35 mm^2s^{-1} (centistokes), at 25°C, more preferably from about 18 mm^2s^{-1} (centistokes) to about 30 mm^2s^{-1} (centistokes). By "average viscosity" is meant that the non-volatile silicone fluid component can have one or more non-volatile silicone fluids outside of the specified range of 10 to 50 mm^2s^{-1} (centistokes), but the overall, i.e., the weighted average, viscosity should be within said range. Viscosity can be measured by a Brookfield® cone and plate viscometer, or other suitable method. By "non-volatile" silicone fluid, as is well known and understood in the art, is meant that the silicone fluids of which the non-volatile silicone fluid component is comprised are not

readily vaporizable (i.e., they do not exhibit an appreciable vapor pressure) at ambient temperatures (particularly at 20°C to 25°C).

The non-volatile silicone fluids that may be used in the present compositions include polyalkyl siloxanes, polyalkylaryl siloxanes, and polyether siloxane copolymers, and mixtures thereof. Preferred non-volatile silicone fluids are linear polyalkyl siloxanes, especially linear polydimethyl siloxanes (i.e., dimethicone). These siloxanes are available, for example, from the General Electric Company (Silicone Products Division, Waterford, NY, USA) in the Viscasil™ series and from Dow Corning Corporation (Midland, Michigan, USA), as the Dow Corning 200 Fluid series.

Other non-volatile silicone fluids that can be used include polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Fluid.

A polyether siloxane copolymer that may be used is, for example, a dimethyl polyoxyalkylene ether copolymer fluid. Such copolymers are available, for example, from the General Electric Company as SF-1066 organosilicone surfactant.

The non-volatile silicone fluid component is present in the compositions hereof in an amount ranging from 25% to 75%, preferably from 35% to 70%, more preferably 45% to 65% of the composition.

Another essential component of the present compositions is a suspension agent. Such suspension agent is present at a level of from 1% to 15%, preferably from 2% to 8%.

Clays and colloidal pyrogenic silica pigments are the preferred materials for use as suspension agents. Colloidal silica is available commercially as Cab-O-Sil® (RTM), a submicroscopic particulated pyrogenic silica.

Clay suspension agents suitable for use in the compositions of the present invention are selected from the group consisting of montmorillonite clays and hydrophobically treated montmorillonite clays. Montmorillonite clays are those which contain the mineral montmorillonite and are characterized by having a suspending lattice. Examples of these clays include the bentonites, hectorites, and colloidal magnesium aluminum silicates. Clay materials are typically made hydrophobic by treatment with a cationic surfactant, such as quaternary ammonium cationic surfactants (e.g., ditallow dimethyl ammonium chloride, i.e., quaternium-18).

Bentonite is colloidal, hydrated aluminum silicate obtained from montmorillonite and has the formula $Al_2O_3 4SiO_2 H_2O$. A more detailed discussion of bentonites can be found in the *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd. ed., Vol 3(1964), pp 339-360, published by Interscience Publishers.

Hectorite, also a montmorillonite clay, differs from bentonite in that there is almost a complete substitution of aluminum in the lattice structure of bentonite by magnesium. In addition, hectorites contain lithium and fluorine. Laponite™ is an example of a commercially available synthetic hectorite marketed by Laporte Industries, Ltd.

The magnesium aluminum silicates are complexes of colloidal magnesium aluminum silicate richer in magnesium than aluminum. Magnesium aluminum silicates are commercially available as Veegum™ (R. T. Vanderbilt Co.).

Preferred clay suspension agents for use in the present invention include hydrophobically treated montmorillonite clays, e.g., hydrophobic bentonites available under the tradename of Bentone™. Bentone™ is prepared by reacting bentonite in a cation exchange system with an amine. Different amines are reacted to obtain a variety of Bentones, which may also differ in proportions of SiO_2, MgO and Al_2O_4. Specific examples of Bentones™ within the scope of the present invention are Bentone™ 38, Bentone™ 34, Bentone™ 27, Bentone™ 14, and Bentone™ LT, all of which have a particle size of below 5 µm (microns) and are commercially available from the NL Industries, Inc.

The compositions that utilize hydrophobically-treated hectorite and bentonite clays to suspend the antiperspirant active material will also generally include a clay activator. Many such clay activators, as well as the levels of use in liquid antiperspirant compositions, are known in the art. Such activating materials include, for example, propylene carbonate, ethanol, and mixtures thereof. Typically, the level of clay activator will be from 25% to 75% of the weight of the clay, more typically from 40% to 60% of the weight of the clay.

The present antiperspirant composition may comprise optional emollients such as volatile silicone fluids as well as non-silicone emollients such as mineral oil, paraffin oils, etc. To minimize any incidence of skin irritation, the compositions contain less than 5% by weight of skin-irritating emollients. Such optional emollients may be included for a variety of reasons, including both cost-saving, and cosmetic purposes. In particular, it may be desirable to include a low amount of mineral oil or other paraffinic oil.

Typical volatile silicone materials include, but are not limited to, D4-D5 cyclomethicones, phenethyl pentamethyl disiloxane, and mixtures thereof. Volatile dimethicone fluid is also contemplated herein.

The compositions of the present composition may also comprise a number of non-emollient optional components to provide cosmetic or aesthetic benefits. For example, preservatives, deodorant actives, such as anti-microbials or bacteriocides, perfumes, coloring agents, fillers, dyes and thickeners may be used. Suitable thickening agents include carboxymethyl cellulose, and polyethylene powder, such as Microthene® (RTM) powder, a polyethylene powder manufactured by U.S.I. Chemicals (New York, New York, USA), having a mean particle diameter of less than 20 µm (microns).

These optional components should be chosen so as not to unduly interfere with the antiperspirant efficacy and the composition stability. Such optional components are generally present in the compositions of the present invention at a level of from 0.01% to 20% by weight.

The present compositions are preferably in the form of a low-viscosity roll-on liquid. However, the present invention may be applicable to other liquid antiperspirant product types, such as aerosol sprays. Products formulated as aerosols

will also comprise a propellant material. Any of the commonly used propellants in the antiperspirancy art are suitable. The propellant can be any liquefiable gas conventionally used for aerosol containers. Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethylether, propane, butane and isobutane, used singly or admixed. Isobutane, used singly or admixed with other hydrocarbons, is preferred.

The amount of the propellant gas is governed by normal factors as are well known in the aerosol art. The composition described previously herein serves as the concentrate and comprises from 5% to 80%, preferably 7% to 45%, more preferably from 20% to 40%, of the total aerosol composition while the propellant comprises from 20% to 95%, preferably from 55% to 93%, more preferably from 60% to 80%.

If a propellant such as dimethylether utilizes a vapor pressure suppressant (e.g., trichloroethane or dichloromethane) the amount of suppressant is included as part of the propellant.

Although the non-volatile silicone or other silicone fluid, or fluid emollient (such as paraffinic oil) may suitably serve as a carrier liquid in the compositions hereof, additional materials may also be used, particularly in the case of aerosol compositions. The carrier liquid can aid efficacy by keeping the antiperspirant compound in contact with the skin so that it does not rub off or wash off. Examples of additional materials are carboxylic esters like isopropyl myristate and isopropyl palmitate; alcohols such as lauryl alcohol, hexadecyl alcohol, and oleyl alcohol; carboxylic acids such as lauric and oleic acid; and lanolin and its derivatives such as acetylated lanolin. Other operable carrier liquids are more hydrophilic than the above-mentioned compounds, for example, organic compounds containing multiple ester groups. This includes, but is not limited to, diesters of dibasic organic acids. Examples of compounds containing multiple ester groups that are suitable for the instant invention are di-n-butyl phthalate, diethyl sebacate, diisopropyl adipate, and ethyl ethylcarbomethyl phthalate [ortho $C_2H_5OOC\cdots O\cdots COOCH_2COOC_3H_5$].

Still other operable carrier liquids are even more hydrophilic than these esters. Among them are polyethylene glycol monolaurate and butoxy-polyoxyethylene oxypropylene glycols (the Ucon 50 HB series; trade mark -- Union Carbide).

Among these various carrier liquids, carboxylic esters having from 12 to 16 carbon atoms are preferred. As described *supra*, they can be either aliphatic or aromatic and can contain either one ester group or multiple ester groups. Especially preferred are di-n-butyl phthalate, diethyl sebacate, diisopropyl adipate, isopropyl myristate and ethyl ethylcarbomethyl phthalate.

These additional carrier liquids, if used, will typically be present in amounts from 1% to 15% of the total aerosol composition.

The present compositions may also contain low levels of high molecular weight polymers similar to those described in US-A-4,152,416, May 1, 1979 to Spitzer et al., especially in the case of aerosol compositions. These polymeric materials are used at a level of from 0.005% to 5% of the total aerosol composition. A preferred material is polyvinylisobutyl ether.

The antiperspirant compositions of the present invention may be manufactured using methods known in the art. In making the compositions, the antiperspirant composition ingredients are typically well-mixed and milled. Aerosol propellant, if applicable, can be included according to standard industry practices. The remaining components are then added to the composition using conventional formulation methods.

The present invention also provides methods for treating or preventing perspiration and malodor associated with human underarm perspiration. These methods comprise applying a safe and effective amount of the liquid antiperspirant compositions of the present invention to the skin in the axillary area of a human. The term a "safe and effective amount" as used herein, is an amount which is effective in eliminating or substantially reducing the production of perspiration which ultimately generates the malodors detected through formation of pungent fatty acids, while being safe for human use at a reasonable risk/benefit ratio.

The liquid antiperspirant compositions of the present invention provide excellent cosmetic attributes both on application and throughout use. They are non-sticky, non-greasy, and provide a dry feel upon application to the skin. The compositions have low incidence of staining of clothes. In addition, the present compositions do not leave substantial levels of white, chalky residue on skin upon dry down, have relatively low incidence of rub-off, and facilitate maintanance of the antiperspirant active material on the skin throughout the in-use period.

The following examples illustrate the present invention. It will be appreciated that other modifications of the present invention within the skill of those in the antiperspirant formulation art can be undertaken without departing from the spirit and scope of this invention.

All parts, percentages, and ratios herein are by weight unless otherwise specified.

Examples 1-2

The following compositions are liquid antiperspirant compositions that are useful for roll-on application and are representative of the present invention.

Component	Example Number (Wt. %)	
	1	2
Dimethicone (20 cs) (20 mm^2s^{-1})	62.7	43.9
Dimethicone (50 cs) (50 mm^2s^{-1})		8.8
Light mineral oil (about 20 cs) (20 mm^2s^{-1}) at 25°C)		10.0
Bentone™-38 Clay [1]	3.5	3.5
Propylene Carbonate	1.6	1.6
Polyethylene powder [2]	4.0	
ZAG antiperspirant active	26.7	26.7
Perfume	0.02	0.02

[1] A quaternium-18 treated hectorite clay available from NL Chemicals Division of NL Industries, Inc. (Hightstown, NJ, USA)

[2] Microthene® polyethylene powder, particle diameter less than about 20 microns, available from U.S.I. Chemicals (New York, NY, USA).

The composition is prepared as follows. The dimethicone material or materials are added to a batch tank, followed by the mineral oil, polyethylene powder and then the Bentone 38 clay, and then mixed for 10 minutes with a rotary mixer. The propylene carbonate is added and the mixture is mixed for an additional 5 minutes. The ZAG antiperspirant active is added and the mixture is mixed for another 10 minutes. Perfume is added and the mixture is mixed for 5 additional minutes. The batch of this liquid is milled to about 750 cps and added to conventional roll-on bottles known in the art. The liquid composition can then be applied to the underarm skin of a human to effectively inhibit perspiration and underarm malodor resulting from perspiration.

The antiperspirant composition provides excellent antiperspiracy efficacy with good product aesthetics and in-use characteristics, including low skin irritation.

Examples 3-4

Aerosol antiperspirant compositions are prepared by first preparing the liquid antiperspirant compositions of Examples 1 (Example 3) and Example 2 (Example 4), as the aerosol antiperspirant concentrates, and are then combined with A-46 volatile aerosol propellant (87% isobutane/13% propane) in a conventional aerosol container. Each of the aerosol compositions contains 70% of the aerosol propellant and 30% of the aerosol antiperspirant concentrate.

Claims

1. A liquid antiperspirant composition characterized in that it comprises:

   (a) from 10% to 70%, by weight, of an antiperspirant active material;
   (b) from 1% to 15%, by weight, of a suspension agent component;
   (c) from 0% to less than 5% by weight, of a volatile silicone fluid; and
   (d) from 25% to 75%, by weight, of a non-volatile silicone fluid having a viscosity of from 10 mm^2s^{-1} (centistokes) to 50 mm^2s^{-1} (centistokes) at 25°C.

2. A liquid antiperspirant as in Claim 1, wherein the antiperspirant active material is a zirconium aluminum complex.

3. A liquid antiperspirant as in Claim 2, wherein the nonvolatile silicone fluid is a polyalkyl siloxane.

4. A liquid antiperspirant as in Claim 3, wherein said nonvolatile silicone fluid comprises dimethicone.

5. A liquid antiperspirant as in Claim 4, wherein the amount of the antiperspirant active material is from 15% to 60%, the amount of the volatile silicone fluid is from 0% to 5%, and the amount of the nonvolatile silicone fluid is from 35% to 70%, preferably from 45% to 65% by weight.

6. A liquid antiperspirant as in Claim 1, 2, 3, 4, or 5 further comprising from 1% to 12%, by weight, of a non-volatile paraffinic oil.

7. A liquid aerosol antiperspirant composition characterized in that it comprises:

I. from 5% to 80%, by weight of the composition, of an antiperspirant concentrate comprising:

(a) from 10% to 70%, weight of the concentrate, of an antiperspirant active material, preferably a zerconium aluminum complex;
(b) from 1% to 15%, by weight of the concentrate, of a suspension agent component;
(c) from 0% to less than 5% by weight of the concentrate, of a volatile silicone fluid; and
(d) from 25% to 75%, by weight of the concentrate, of a non-volatile silicone fluid, preferably a polyalkyl siloxane or dimethicone or a mixture thereof, having a viscosity of from 10 mm^2s^{-1} (centistokes) to 50 mm^2s^{-1} (centistokes) at 25°C; and

II. from 20% to 95%, by weight of the composition, of an aerosol propellant.

8. A liquid antiperspirant as in Claim 7, wherein said nonvolatile silicone fluid has a viscosity of from 15 mm^2s^{-1} to 35 mm^2s^{-1}, preferably from 18 mm^2s^{-1} (centistokes) to 30 mm^2s^{-1} (centistokes) at 25°C.

9. A liquid antiperspirant as in Claim 7 or 8, further comprising from 0.1% to 15%, by weight, of a non-volatile paraffinic oil.

Patentansprüche

1. Flüssige, schweißhemmende Zusammensetzung, dadurch gekennzeichnet, daß sie

(a) 10 bis 70 Gew.-% eines schweißhemmend wirksamen Materials;
(b) 1 bis 15 Gew.-% einer Suspensionsmittel-Komponente;
(c) 0 bis weniger als 5 Gew.-% eines flüchtigen Silikonfluids; und
(d) 25 bis 75 Gew.-% eines nichtflüchtigen Silikonfluids mit einer Viskosität von 10 mm^2s^{-1} (centistokes) bis 50 mm^2s^{-1} (centistokes) bei 25° C,

umfaßt.

2. Flüssiges schweißhemmendes Mittel nach Anspruch 1, wobei das schweißhemmend wirksame Material ein Zirkonium-Aluminium-Komplex ist.

3. Flüssiges schweißhemmendes Mittel nach Anspruch 2, wobei das nichtflüchtige Silikonfluid ein Polyalkylsiloxan ist.

4. Flüssiges schweißhemmendes Mittel nach Anspruch 3, wobei das nichtflüchtige Silikonfluid Dimethicon umfaßt.

5. Flüssiges schweißhemmendes Mittel nach Anspruch 4, wobei die Menge des schweißhemmend wirksamen Materials 15 bis 60 Gew.-%, die Menge des flüchtigen Silikonfluids 0 bis 5 Gew.-% und die Menge des nichtflüchtigen Silikonfluids 35 bis 70 Gew.-%, vorzugsweise 45 bis 65 Gew.-%, betragen.

6. Flüssiges schweißhemmendes Mittel nach Anspruch 1, 2, 3, 4 oder 5, umfassend weiterhin 1 bis 12 Gew.-% eines nichtflüchtigen paraffinischen Öls.

7. Flüssige schweißhemmende Aerosol-Zusammensetzung, dadurch gekennzeichnet, daß sie

I. 5 bis 80 Gew.-% der Zusammensetzung eines schweißhemmenden Konzentrats, umfassend:

(a) 10 bis 70 Gew.-% des Konzentrats eines schweißhemmend wirksamen Materials, vorzugsweise ein Zirkonium-Aluminium-Komplex;

(b) 1 bis 15 Gew.-% des Konzentrats einer Suspensionsmittel-Komponente;
(c) 0 bis weniger als 5 Gew.-% des Konzentrats eines flüchtigen Silikonfluids; und
(d) 25 bis 75 Gew.-% des Konzentrats eines nichtflüchtigen Silikonfluids, vorzugsweise ein Polyalkylsiloxan oder Dimethicon oder eine Mischung hiervon, mit einer Viskosität von 10 mm^2s^{-1} (centistokes) bis 50 mm^2s^{-1} (centistokes) bei 25° C; und

II. 20 bis 95 Gew.-% der Zusammensetzung eines Aerosol-Treibmittels,

umfaßt.

8. Flüssiges schweißhemmendes Mittel nach Anspruch 7, wobei das nichtflüchtige Silikonfluid eine Viskosität von 15 mm^2s^{-1} bis 35 mm^2s^{-1}, vorzugsweise 18 mm^2s^{-1} (centistokes) bis 30 mm^2s^{-1} (centistokes) bei 25° C besitzt.

9. Flüssiges schweißhemmendes Mittel nach Anspruch 7 oder 8, umfassend weiterhin 0,1 bis 15 Gew.-% eines nichtflüchtigen paraffinischen Öls.

Revendications

1. Composition d'antitranspirant liquide, caractérisée en ce qu'elle comprend:

(a) de 10% à 70% en poids d'une substance active antitranspirante;
(b) de 1% à 15% en poids d'un constituant agent de mise en suspension;
(c) de 0% à moins de 5% en poids d'une huile de silicone volatile; et
(d) de 25% à 75% en poids d'une huile de silicone non volatile ayant une viscosité de 10 mm^2s^{-1} (centistokes) à 50 mm^2s^{-1} (centistokes), à 25°C.

2. Antitranspirant liquide selon la revendication 1, dans lequel la substance active antitranspirante est un complexe de zirconium et d'aluminium,

3. Antitranspirant liquide selon la revendication 2, dans lequel l'huile de silicone non volatile est un polyalkylsiloxane.

4. Antitranspirant liquide selon la revendication 3, dans lequel ladite huile de silicone non volatile comprend de la diméthicone.

5. Antitranspirant liquide selon la revendication 4, dans lequel la quantité de la substance active antitranspirante est de 15% à 60%, la quantité de l'huile de silicone volatile est de 0% à 5%, et la quantité de l'huile de silicone non volatile est de 35% à 70%, de préférence de 45% à 65%, en poids.

6. Antitranspirant liquide selon la revendication 1, 2, 3, 4 ou 5, comprenant, en outre, de 1% à 12%, en poids, d'une huile paraffinique non volatile.

7. Composition d'antitranspirant liquide en aérosol, caractérisée en ce qu'elle comprend:

I. de 5% à 80%, en poids de la composition, d'un concentré antitranspirant comprenant:

(a) de 10% à 70%, en poids du concentré, d'une substance active antitranspirante, de préférence d'un complexe de zirconium et d'aluminium;
(b) de 1% à 15%, en poids du concentré, d'un constituant agent de mise en suspension;
(c) de 0% à moins de 5%, en poids du concentré, d'une huile de silicone volatile; et
(d) de 25% à 75%, en poids du concentré, d'une huile de silicone non volatile, de préférence d'un polyalkylsiloxane ou d'une diméthicone, ou d'un mélange des deux, ayant une viscosité de 10 mm^2s^{-1} (centistokes) à 50 mm^2s^{-1} (centistokes), à 25°C; et

II. de 20% à 95%, en poids de la composition, d'un propulseur d'aérosol.

8. Antitranspirant liquide selon la revendication 7, dans lequel ladite huile de silicone non volatile possède une viscosité de 15 mm^2s^{-1} à 35 mm^2s^{-1}, de préférence de 18 mm^2s^{-1} (centistokes) à 30 mm^2s^{-1} (centistokes), à 25°C.

9. Antitranspirant liquide selon la revendication 7 ou 8, comprenant, en outre, de 0,1% à 15% en poids d'une huile paraffinique non volatile.

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(71) Applicant: **Società Italo-Britannica L. Manetti-H. Roberts & C. S.p.A.**
50123 Firenze (IT)

(72) Inventors:
- **Mucci, Paolo**
  50100 Firenze (IT)
- **Meucci, Sandro**
  50100 Firenze (IT)
- **Ceccarelli, Luigi**
  25036 Palazzolo Sull'Oglio, (Brescia) (IT)

(74) Representative: **Bardini, Marco Luigi et al**
c/o Società Italiana Brevetti S.p.A.
Corso dei Tintori, 25
50122 Firenze (IT)

(54) Deodorant and/or moisturizing cosmetic composition

(57) A deodorant and/or moisturizing cosmetic composition formed by an emulsion oil in water, comprising: a) a combination of two or more deodorant and/or moisturizing active ingredients, b) an orthophosphonic acid ester in an amount comprised between 0.3 and 7%, and c) a watersoluble resin consisting of a homopolymer of the acrylic acid in an amount comprised between 0.05% and 1.5%, said composition having a viscosity at 20°C comprised between 800 and 10000 caps. The main advantage of the cosmetic composition according to the invention consists in that it is a cream and, at the same time, is vaporizable, as the viscosity is always comprised in the above stated range.

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Description

[0001] The present invention relates to a deodorant and/or moisturizing cosmetic composition.

[0002] The problem of the deodoration of human body has been tackled in several ways with products of different forms and compositions. In particular, the deodorant product may be made available in the solid form, as a cream or as a liquid. Different ways of application also correspond to the different forms. The stick is used for products available in the solid form, while the roll-on or the direct product massaging are the most common application modes when the product is available as a cream. Aerosol, vaporizers or spray dispensers are used when the products are in the liquid form.

[0003] The vaporizable liquid deodorants are comprised within the wide group of cosmetic deodorants and comprise commercially available preparations containing antiperspirant substances, other active ingredients, fragrance, essential oils, etc. with or without alcohol.

[0004] Vaporizable liquid deodorants are also known containing emollient substances of various origin, to improve the moisturizing properties of the product and make it specially delicate and tolerable for the skin. The viscosity of these products is similar to that of water.

[0005] Deodorants products defined as deodorant cleansing lotion or deodorant cream are also commercially available in the form of a liquid emulsion. They have a milky white color which could give the impression that they are softer and more delicate products than the transparent liquid products, but they have in any case a liquid consistency: therefore, particularly for this type of liquid product, which requires some time to dry, the inconvenience has been found that it can trickle down the body.

[0006] On the other hand, the deodorants in the form of a cream, which have a viscosity high enough that the use of a tube container or the roll-on is allowed, are applied in the above mentioned ways, i.e. through massaging in the case of the cream contained in a tube or directly by means of the roll-on.

[0007] Furthermore, due to the higher viscosity of the cream product, it may happen that the body part, which the product has been applied on, remains tacky and slightly oily, with an unpleasant feeling for the user and problems, for example, of soiling the clothes; it may be also necessary to wash the hands after the product has been applied.

[0008] The features of the prior art products and compositions do not allow for a deodorant and/or moisturizing product to be obtained as a stable cream suitable of being vaporized. It is therefore an object of the present invention to provide a deodorant and/or moisturizing product having a cream consistency and, at the same time, suitable of being vaporized, thus overcoming the above mentioned prior art incoveniences.

[0009] The above result has been achieved by the deodorant and/or moisturizing cosmetic composition according to the invention consisting by an oil-in-water emulsion, characterized in that it comprises:

a) a combination of two or more deodorant and/or moisturizing active ingredients,
b) an ester of the ortophosphoric acid in an amount comprised between 0.3% and 7%,
c) a water-soluble resin consisting of an acrylic acid homopolymer in an amount comprised between 0.05% and 1.5%,

and further characterized in that the viscosity at 20°C is comprised between 800 and 10000 cps.

[0010] The deodorant and/or moisturizing cosmetic composition according to the invention consists, therefore, of a deodorant and/or moisturizing product in the form of a fluid cream of medium/low viscosity, capable of being vaporized.

[0011] The essential advantage of the deodorant and/or moisturizing cosmetic composition according to the present invention consists in that it is costantly in the form of a cream and, at the same time, is vaporizable, as its viscosity at 20°C is always comprised in the above mentioned range and, even if small variations may occur, it never falls below 800 cps nor goes beyond 10000 cps at least during the first three months.

[0012] A further object of the invention is the use of the above mentioned cosmetic composition as a body deodorant and/or moisturizing product.

[0013] In particular, the deodorant and/or moisturizing cosmetic composition according to the invention can be used, thanks to its features, as a deodorant and/or moisturizing product for armpits, feet and other body parts requiring deodorizing and/or moisturizing.

[0014] The oil-in-water emulsion, which is the basis of the deodorant and/or moisturizing cosmetic composition according to the present invention, can be used also as a basis for creamy and vaporizable deodorant and/or moisturizing cosmetic compositions, containing further active ingredients such as emollients, preservatives, antioxidants, moisturizing/humectant substances and/or perfume.

[0015] Such moisturizing components allow to obtain a product in which the moisturizing property is enhanced for skins with increased need in this respect.

[0016] Moreover, the cosmetic composition as a vaporizable cream according to the invention can be advantageously used for further applications, such as, for example, a balsam, an emollient product, etc., if the combination of two or more deodorant and/or moisturizing active ingredients is partially or completely replaced by other active ingredients suitably selected according to the product to be obtained.

[0017] All the percentages given in the present specification have to be construed as weight percentages with respect to the total weight of the composition, unless otherwise specified.

[0018] The combination of deodorant and/or moislur-

izing active ingredients of the deodorant and/or moisturizing cosmetic composition of the present invention can be any combination of the following compounds: vitamin E acetate (toco-pheril acetate), farnesol (3,7, 11-trimethyl-2,6, 10-dodecatrien-1-ol), triethyl citrate, C_{12}-C_{13} alkyl-lactate or C_{12}-C_{13} alkyl citrate, denatured ethyl alcohol, triclosan (2,4,4'-trichloro-2'-hydroxydiphenil ether) L-arginine or arginine-PCA as deodorant active ingredients, and/or sodium pyroglutamate, sodium lactate, proteic hydrolysates (collagenic or cheratinic), reconstituted aminoacid mixtures, saccharidic components (glucose, fructose, mucopolysaccharides, etc.), polyalcohols (glycerole, sorbitole) and glycols (polyethylenglycol), as moisturizing active ingredients.

[0019] The combination of the deodorant and/or moisturizing active ingredients can be a combination of C_{12}-C_{13} alkyl lactate (or C_{12}-C_{13} alkyl citrate) in an amount not higher than 4%, Farnesol in an amount not higher than 1.5% and vitamin E acetate in an amount not higher than 1.5%. The combination may also comprise triethyl citrate in an amount not higher than 4% and/or denatured ethyl alcohol in an amount not higher than 10%.

[0020] The ester of the ortophosphoric acid is preferably a mixture of mono-, bi- and triesters of the ortophosphoric acid with alkyl tetraglycolethers, where the alkyl group is mainly a mixture of C_{12} and C_{14}.

[0021] The ester of the ortophosphoric acid can be the trilauril (4) OE phosphate.

[0022] These products can be used at room temperature and exhibit an high emulsifying activity, mainly in the presence of paraffin oils and/or synthetic oils.

[0023] A commercial product known as Hostapath KL 340 N, corresponding to the trilauril (4) OE phosphate, is preferably used as ester of the ortophosphoric acid. The water-soluble resin of the deodorant and/or moisturizing cosmetic composition according to the present invention, consisting of an acrylic acid homopolymer, i. e. carboxypolymethylene, is commercially available under the name Carbopol 5/984.

[0024] The acrylic acid homopolymers exhibit a viscosity-increasing and stabilizing action on the emulsions: this component is used not only to make the emulsion thicker, but also in view of its ability to impart a slipping coefficient to the emulsion.

[0025] The presence of both the orthophosphoric acid ester and the water-soluble resin is essential for the preparation of a deodorant and/or moisturizing cosmetic composition capable of being easily pumped, with a low resistance to handling.

[0026] As set forth previously, the deodorant and/or moisturizing cosmetic composition according to the present invention comprises a combination of two or more deodorant and/or moisturizing active ingredients.

[0027] In particular, vitamin E acetate can be present in an amount comprised between O and 1.5% approx. and is added to the deodorant and/or moisturizing cosmetic composition according to the present invention even for its antioxidant properties. Vitamin E protects the skin by preventing free-radicals formation and, at the same time, maintains it moist, in view of the fact that reduces the loss of water.

[0028] Farnesol (3,7, il-trimethyl-2,6,10-dodecontrien-1-ol) is a natural-like bacteriostatic agent and can be added in an amount comprised between about 0 and 1.5% and exhibits an inhybitory action against bacterial growth and degradation, which are responsible for the formation of malodour. It can be found in the essential oils of many natural products.

[0029] Triethyl citrate can be present alone or in combination with buthyl-hydroxy-toluene (BHT), an antioxidant agent, in an amount comprised between about 0 and 4%. Triethyl citrate exhibits a deodorizing action as prevents the enzymatic decomposition of the fatty acids contained in the sweat, due to microorganisms usually present on the skin. In this way, malodorous degradation products do not form and the physiologic perspiration process is not altered.

[0030] BHT, which, as said above, is an antioxidant, acts synergistically with triethyl citrate to prevent the decomposition of some insaturated fatty acids of the skin into malodorous substances.

[0031] The triethyl citrate to be used is preferably the commercial product named Citrogen-Deo.

[0032] BHT can be present in the composition according to the present invention in an amount comprised between about 0 and 1%.

[0033] As already stated, another possible deodorant active ingredient is C_{12}-C_{13}-alkyl lactate which is added in an amount comprised between about 0 and 4%. This ingredient is very important for its considerable, marked deodorant properties, having also a slightly bacteriostatic effect; such ingredient also develops a dermoprotective action if it is associated to antibacterial agents, thanks to its emollient and moisturizing properties. The agent is commercially available under the name Cosmacol ELI. Furthermore, being a lactic acid carrier, it has many properties of the fruit acids, but differently to them, its action is extremely soft, i.e. without unwanted side effects. Therefore, it can be used even in products for the most delicate skins.

[0034] In the place of, or in addition to, C_{12}-C_{13} alkyl lactate there can be used another deodorant/emollient active ingredient of the same family of the previous one, i.e. the C_{12}-C_{13} alkyl citrate, a triester of the citric acid with the C_{12}-C_{13} monobranched alcohol. This ester is a citric acid carrier, an α-hydroxyacid (AHA) with particular emollient and antioxidant properties, and is known commercially as Cosmacol ECI and can be added in an amount comprised between 0 and 1%.

[0035] The denatured ethyl alcohol can be added to an amount comprised between 0 and 10% and increases the feel of freshness, enhancing at the same time the bacteriostatic action of the composition.

[0036] A further active ingredient which can be used in the composition according to the invention is the triclosan (2,4,4'-trichloro-2'-hydroxydiphenil ether) . Tri-

closan is a wide-spectrum antibacterial agent which is active against bacteria (Gram+, Gram-, leavens and moulds) responsible for sweat degradation and therefore for the malodour formation. It exhibits a good skin tolerability and is compatible with the other ingredients. It is commercially available under the name of DP300 and can be added in an amount up to 0.3%.

[0037] L-arginine and arginine-PCA (a compound of arginine and pyrrolidon carboxylic acid exhibit deodorant properties thanks to their antioxidant activity like vitamin E. They also exhibit moisturizing properties because they can retain water on the skin surface.

[0038] The above mentioned moisturizing active ingredients prevent skin dehydratation phenomena from one side and restore, at least at the corneous level, the normal conditions of hydratation, softness and elasticity from the other side.

[0039] The moisturizing and deodorant cosmetic composition according to the invention may contain preferably sodium pyroglutamate in an amoount comprised between 0 and 5%.

[0040] Sodium pyroglutamate is a substance contained in a large amount in the corneous layer of the skin (it is one of the components of the natural moisturizing factor - NMF) and is used as moisturizing active ingredient in view of its high hygroscopicity which increases the water content of the skin and gives elasticity and softness to it. This substance is commercially available under the name Adjdew NL-50.

[0041] The composition according to the present invention may also contain propylene glycol as moisturizing/humectant active ingredient in an amount comprised between about 0 and 7%.

[0042] As previously stated, the deodorant and moisturizing composition according to the present invention may comprise other components.

[0043] For example, it may comprise an emollient ingredient which can be selected from triglycerides of fatty acids of natural origin and vaselin oil.

[0044] In particular, among the emollient ingredients particularly preferred is a triglyceride of fatty acids of natural origin, i.e. the caprilic/capric triglyceride, commercially known as Myritol 812, in an amount comprised between about 3 and 7%.

[0045] It exhibits a good dermatological compatibility and a good solubilizing power against liposoluble additives.

[0046] The vaseline oil may be present in an amount comprised between 5 and 10%.

[0047] The deodorant and moisturizing cosmetic composition according to the present invention may also contain a preservative preferably consisting of a mixture of diazolidinil urea and paraben (parahydroxybenzoic acid esters).

[0048] The commercial name of the preferred preservative according to the present invention is Germaben II. It consists of a mixture of propylene glycol, diazolidinil urea, methylparaben and propylparaben and is present in an amoount comprised between 0 and 2%. The deodorant and moisturizing cosmetic composition according to the present invention may also contain an antioxidant which may be butyl-hydroxy-toluene (BHT) and/or sodium EDTA.

[0049] Sodium hydroxyde is used to neutralize the homopolymer of the acrylic acid and is added in an amount proportional to it.

[0050] Disodium EDTA is used as complexing agent of the calcium and magnesium salts present in water, when not fully deionized water is used. The deodorant and/or moisturizing cosmetic composition according to the invention can also contain a perfume in an amount comprised between about 0 and 5%.

[0051] The main advantage of the deodorant and/or moisturizing cosmetic composition according to the present invention consists in that it is an emulsion with the appearance of a, more or less viscous, but not liquid, fluid cream, having a deodorant and/or moisturizing effect, capable of being vaporized by means of a micropump. Therefore, the product has, at the same time, the advantage of the cream product (for example, it does not trickle down the armpits after its application, before drying) and of the vaporizable product (there is no need to spread the product with the fingers or by means of the roll-on). Therefore, the application of the product is extremely practical and pleasant for the user, because it is fluid enough to be capable of being vaporized and at the same time viscous enough not to trickle down the armpits and the body.

[0052] A further advantage of the cosmetic composition according to the present invention is to be a viscous cream exhibiting at the same time moisturizing, emollient and deodorant action.

[0053] The features and advantages of the composition according to the invention will be better understood from the following detailed exemplifying description.

Example 1

Method for preparing a deodorant and/or moisturizing cosmetic composition in the form of a vaporizable cream

[0054] The deodorant and/or moisturizing cosmetic composition according to the present invention is prepared as follows.

[0055] Vaseline oil, Myritol 312, Hostapath KL 340 N, Cosmacol ELI, Farnesol, triethyl citrate, perfume, vitamin E acetate, Germaben II and BHT (i.e. the selected deodorant active ingredients, the ester of the ortophosphoric acid, an antioxidant, an emollient, a preservative and perfume) were introduced in a stainless steel reactor. The mixture was stirred until a complete dissolution is reached.

[0056] Water, propylene glycol, disodium EDTA, Carbopol 5/984 (i.e. water, the water-soluble resin, a humectant agent and an antioxidant) were introduced in a second stainless steel reactor equipped with an homog-

enizer and the mixture was homogenized up to a complete dispersion of the Carbopol 5/984.

[0057] The two mixtures obtained in this way were then combined together. Sodium hydroxyde, which was previously solubilized in water, was added under slow stirring and the resulting mixture was stirred and homogenized until a fluid and smooth emulsion is obtained.

[0058] If moisturizing active ingredients, such as sodium pyroglutamate, are present, these are added preferably at the end of the above described operation. Then, once the fluid and smooth emulsion is obtained, the moisturizing agent is added and the mixture is stirred up to dissolution.

[0059] The formulation prepared in this way has the following specifications:

Appearance: white homogeneous emulsion;
Density (20°C): 0.980 - 0.990;
Viscosity (20°C): 800-10000 cps (Brookfield-TB wheel - 5rpm) measured after 18 hours;
Reaction: pH 5.0 - 7.0;
Stability: no separation occurs;
Total microbial counting: lower than 100 UFC/ml.

Example 2

[0060] A deodorant and/or moisturizing cosmetic composition in the form of a vaporizable cream was prepared as described in example 1, with the components listed in the following table:

Components	Weight %
Water	74,876
Vaseline Oil	8,000
Propylene Glycol	5,000
Myritol 312	5,000
Hostaphat KL 340 N	3,000
Cosmacol ELI	1,000
Perfume	1,000
Farnesol	0,600
Vitamin E acetate	0,500
Germaben II	0,500
Carbopol 5/984	0,300
Sodium Hydroxide	0,124
Bisodium Salt EDTA	0,050
BHT	0,050

[0061] The viscosity at 20°C (initial) ranges from 2000 cps to 3000 cps.

Example 3

[0062] A deodorant and/or moisturizing cosmetic composition in the form of a vaporizable cream was prepared as described in example 1, with the components listed in the following table:

Components	Weight %
Water	72,170
Vaseline Oil	8,000
Propylene Glycol	5,000
Myritol 312	5,000
Hostaphat KL 340 N	3,000
Triethyl citrate	2,000
Cosmacol ELI	1,000
Perfume	1,000
Farnesol	0,600
Vitamin E acetate	0,500
Germaben II	0,500
Carbopol 5/984	0,800
Sodium Hydroxide	0,330
Bisodium Salt EDTA	0,050
BHT	0,050

[0063] The viscosity at 20°C (initial) ranges from 4000 cpc to 6000 cpc.

Example 4

[0064] A deodorant and/or moisturizing cosmetic composition in the form of a vaporizable cream was prepared as described in example 1, with the components listed in the following table:

Components	Weight %
Water	73,733
Vaseline Oil	8,000
Propylene Glycol	5,000
Myritol 312	5,000
Hostaphat KL 340 N	3,000
Cosmacol ELI	2,000
Perfume	1,000
Farnesol	0,600
Vitamin E acetate	0,500
Germaben II	0,500
Carbopol 5/984	0,330
Sodium Hydroxide	0,137
Triethyl citrate	0,100
Bisodium Salt EDTA	0,050
BHT	0,050

[0065] The viscosity at 20°C (initial) ranges from 2000 cps to 3000 cps.

Example 5

[0066] A deodorant and/or moisturizing cosmetic composition in the form of a vaporizable cream was pre-

pared as described in example 1, with the components listed in the following table:

Components	Weight %
Water	72,733
Vaseline Oil	8,000
Propylene Glycol	5,000
Myritol 312	5,000
Hostaphat KL 340 N	3,000
Cosmacol ELI	2,000
Denatured ethyl alcohol	1,000
Perfume	1,000
Farnesol	0,600
Vitamin E acetate	0,500
Germaben II	0,500
Carbopol 5/984	0,330
Sodium Hydroxide	0,137
Triethyl citrate	0,100
Bisodium Salt EDTA	0,050
BHT	0,050

[0067] The viscosity at 20°C (initial) ranges from 2000 cps to 3000 cps.

Example 6

[0068] A deodorant and/or moisturizing cosmetic composition in the form of a vaporizable cream was prepared as described in example 1, with the components listed in the following table:

Components	Weight %
Water	74,433
Vaseline Oil	8,000
Propylene Glycol	5,000
Myritol 312	5,000
Hostaphat KL 340 N	3,000
Adjdew NL-50	2,000
Perfume	1,000
Vitamin E acetate	0,500
Germaben II	0,500
Carbopol 5/984	0,330
Sodium Hydroxide	0,137
Bisodium Salt EDTA	0,050
BHT	0,050

[0069] The viscosity at 20°C (initial) ranges from 2000 cps to 3000 cps.

Example 7

[0070] A deodorant/moisturizing cosmetic composition in the form of a vaporizable cream is prepared as described in example 1 with the components listed in the following table:

Components	Weight %
Water	75,276
Vaseline Oil	8,000
Propylene Glycol	5,000
Myritol 312	5,000
Hostaphat KL 340 N	3,000
Cosmecol ECI	1,000
Perfume	1,000
Vitamin E acetate	0,500
Germaben II	0,500
Carbopol 5/984	0,300
Irgosan DP 300	0,200
Sodium Hydroxide	0,124
Bisodium Salt EDTA	0,050
BHT	0,050

[0071] The viscosity at 20°C (initial) ranges from 2000 cps to 3000 cps.

Claims

1. Deodorant and/or moisturizing cosmetic composition consisting of an emulsion of oil in water, characterized in that it comprises:

   - a combination of at least two deodorant and/or moisturizing active ingredients;
   - an ortophosphoric acid ester in an amount comprised between 0.3% and 7%;
   - a water-soluble resin consisting of an homopolymer of the acrylic acid in an amount comprised between 0.05% and 1.5%,

   and further characterized in that the viscosity at 20°C is comprised between 800 and 10000 cps.

2. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that it is in the form of a vaporizable cream.

3. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that it also comprises emollient, preservative, antioxidant, moisturizing/humectant ingredients and/or perfume.

4. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that the combination of the deodorant and/or moisturizing active ingredients is any combination of the following substances: vitamine E acetate (tocopheryl ac-

etate), Farnesol (3,7,11-trimethyl-2,6,10-dodecatrien-1-ol), triethyl citrate, C_{12}-C_{13} alkyl lactate, C_{12}-C_{13} alkyl citrate, denatured ethyl alcohol, triclosan (2,4,4'-trichloro-2'-hydroxydiphenil ether), L-arginine and arginine-PCA as deodorant active ingredients, and/or sodium pyroglutamate, sodium lactate, proteic hydrolysates, reconstituted mixtures of aminoacids, saccharidic components, polyalcohols and glycols.

5. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that the combination of the deodorant active ingredients is a combination of C_{12}-C_{13} alkyl lactate in an amount not greater than 4%, Farnesol in an amount not greater than 1.5% and vitamin E acetate in an amount not greater than 1.5%.

6. Deodorant and/or moisturizing cosmetic composition according to claim 5, characterized in that it also comprises triethyl citrate in an amount not greater than 4%.

7. Deodorant and/or moisturizing cosmetic composition according to claim 5, characterized in that it also comprises denatured ethyl alcohol in an amount not greater than 10%.

8. Deodorant and/or moisturizing cosmetic composition according to claim 5, characterized in that it also comprises triethyl citrate in an amount not greater than 4% and denatured ethyl alcohol in an amount not greater than 10%.

9. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that the ester of the orthophosphoric acid is a mixture of mono-, di- and tri-esters of the ortophosphoric acid with alkyl tetraglycol ethers, wherein the alkyl group is mainly a mixture of C_{12}-C_{14}.

10. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that the ester of the ortophosphoric acid is trilauril(4)OE phosphate.

11. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that the acrylic acid homopolymer is carboxypolymethylene (Carbopol 5/984).

12. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that the emollient active ingredient is selected from natural fatty acid triglycerides and vaseline oil.

13. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that the emollient active ingredient is the caprilic/capric triglyceride, in an amount comprised between 3 and 7%.

14. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that the preservative consists of a mixture of diazolidinil urea and parabens.

15. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that the preservative consists of a mixture of propylene glycol, diazolidinil urea, methylparaben and propylparaben in an amount comprised between 0 and 2%.

16. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that the antioxidant can be buthyl-hydroxy-toluene (BHT), sodium hydroxyde, and/or bisodium EDTA.

17. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that it comprises triethyl citrate as deodorant active ingredient and buthyl-hydroxy-toluene as antioxidant.

18. Deodorant and/or moisturizing cosmetic composition according to claim 4, characterized in that the combination of deodorant and/or moisturizing active ingredients comprises sodium pyroglutamate in an amount not greater than 5%.

19. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that the humectant agent is propylene glycol in an amount comprised between 0 and 7% approximately.

20. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that it comprises a perfume in an amount comprised between 0 and 5%.

21. Deodorant and/or moisturizing cosmetic composition according to claim 3, characterized in that it comprises C_{12}-C_{13} alkyl lactate in an amount of 1%, Farnesol in an amount of 0.6%, trilauril (4) OE phosphate in an amount of 3%, vitamin E acetate in an amount of 0.5% and carboxypolymethylene (Carbopol 5/984) in an amount of 0.3%.

22. Deodorant and/or moisturizing cosmetic composition according to claim 1, characterized in that the combination of deodorant active ingredients is a combination of C_{12}-C_{13} alkyl citrate, in amount not higher than 4%, vitamin E acetate in an amount not higher than 1.5% and triclosan in an amount not higher than 0.3%.

23. A deodorant and/or moisturizing cream having the

composition according to any one of the claims 1-22.

24. Use of the deodorant and/or moisturizing cosmetic composition according to any one of the claims 1-22, as a deodorant and/or moisturizing body product.

25. The use according to claim 24, as a deodorant and/or moisturizing product for armpits, feet or other body parts requiring deodorizing or moisturizing.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 83 0439

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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